

Carbon nanotubes and polyaniline supported Pt nanoparticles for methanol oxidation towards DMFC applications

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Abstract A microwave reduction route was employed for the synthesis of Pt nanoparticles supported on multi-walled carbon nanotubes (MWCNT). The as-prepared Pt-MWCNT electrocatalysts were characterized by FT-IR, XRD and TEM analysis. Further, the as-prepared catalysts were probed for its electrocatalytic activity towards methanol oxidation by cyclic voltammetry (CV) in 0.5 M CH₃OH + 0.5 M H₂SO₄ solution. Two kinds of electrocatalysts viz. Pt-MWCNT and Pt-MWCNT/PANI were probed to study the effect of both carbon nanotubes and polyaniline (PANI) towards methanol oxidation. The effect of scan rate, concentration and long-term cycle stability analysis has been investigated in detail. Results show that the presence of MWCNT and PANI improves the electrocatalytic efficiency towards methanol oxidation. Pt-MWCNT/PANI shows high peak current density towards methanol oxidation and good long-term stability even after 600 cycles indicating that the catalyst could be used for practical applications.

Keywords MWCNT · Polyaniline · Methanol oxidation · Fuel cells

Introduction

Investigations aiming at developing efficient fuel cells have contributed greatly to the development of catalysts for the electrooxidation of small organic molecules. Among these molecules, methanol has been the most widely investigated, due to its possible use as a fuel in direct methanol

fuel cells (DMFCs) as it has significant advantages for portable and automobile applications. For example, DMFC does not require a separate hydrogen generation system and methanol is an attractive fuel because it is inexpensive, widely available and can be handled and transported easily (Lim et al. 2008; Liu et al. 2006; Appleby and Foulkes 1989; Arico et al. 2001). Despite these advantages, however, some problems still prevent the commercialization of DMFCs. These problems include the fuel crossover from anode to cathode, the poisoning of platinum catalyst, and the reliability and durability of the membrane electrode assembly (MEA) (Ren et al. 2000; Chu and Jiang 2002). Classical electrocatalysts are often disfavored owing to its low rate in electrocatalytic reactions and thus needs some improvements (Chu and Jiang 2002). Such improvements are necessary with a motivation of lowering of the amount of precious metal that is necessary for economic reasons mainly for applications such as generators for electric vehicles. Decreasing the amount of catalysts could be achieved by decreasing the size of the particles. Hence, a plethora of interest has been generated in the way of developing new and novel catalyst materials. Pt-based catalyst has been developed and probed for its electrocatalytic property (Chen et al. 2009; Zhou et al. 2010; Wang et al. 2010; Zhiani et al. 2010; Wu et al. 2006; Habibi and Pournaghi-Azar 2010; Hoa et al. 2011; Antolinia 2010).

Pt is a potent and widely used electrode for the oxidation of various fuels (Parsons and Vandernoof 1988; Lamy et al. 1997). But the main drawback in using Pt as working electrode is the formation of poisonous intermediate CO_{ads} on the electrode surface (Leger and Lamy 1990). The absence of CO as an intermediate is thus always a desirable characteristic in the fuel cell reactions. A possible alternative to decrease CO_{ads} poisoning is the use of Pt alloyed with other metals (Kristian et al. 2009; Zhao et al. 2010;

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Ishikawa et al. 2000). The utilization of such alloys can provide the generation of oxygen containing species viz OH^- , which provokes the oxidation of strongly adsorbed intermediates such as CO_{ads} to CO_2 . In addition, the choice of a suitable supporting catalyst material is an important factor to be considered. In fact, the choice of a suitable supporting material is an imperative factor that may affect the recital of supported electrocatalysts owing to their interactions and surface reactivity (Uchida et al. 1995). The supporting materials with a high surface area are requisite to disperse catalyst particles and reduce the catalyst loading under the condition of acquiring high catalytic activity. Conductive polymers allow uniform distribution of catalyst particles, which forms the main criteria of electrocatalytic reactions. Such polymers are usually used as host matrixes to incorporate noble metal catalysts for their possible applications in the electrooxidation of small molecules such as hydrogen, methanol, formic acid, etc. (Qu et al. 2010; Huang et al. 2011; Chen et al. 2006; Guo et al. 2009; Gomez and Weaver 1997; Bouzek et al. 2000). Among many conducting polymers, polyaniline has been of particular interest because of its environmental stability, controllable electric conductivity and various redox properties. Polyaniline can have a specific interaction with Pt that helps to reduce the absorbance of CO on Pt particles, which is a major factor leading to the poisoning of Pt catalyst (Lamy et al. 2002). Polyaniline is particularly attractive as a host matrix for confining the active catalyst particles as this medium could provide an efficient route for the shuttling of electronic charges to the catalyst centers. Platinum has a wide range of applications in many fields inspite of its high price. Hence, formulation of electrode that reduces the amount of platinum would be more advantageous economically.

Another good supporting material in fuel cell technology is carbon nanotubes. Attractive properties of nanotubes related with their good electrical conductivity, entanglement and high resiliency have been demonstrated in other electrochemical energy storage systems, e.g., supercapacitors. Many other authors have reported the promising application of carbon nanotubes as a promising catalyst support for cathodic and anodic reactions in fuel cells (He et al. 2004a, b; Guo and Li 2004; Liu et al. 2002; Rajesh et al. 2002). The carbon nanotube material is considered to have several advantages over conventional support materials, which includes (a) having more defined crystalline structure with higher conductivity, (b) containing little impurities, such as metals and sulfides, and thus eliminating potential poisoning effects to electrocatalysts, and (c) possessing three-dimensional structure thus favoring the flow of reactant and providing a large reaction zone when fabricated into electrodes. The carbon nanotubes are also chemically stable and resistant to

thermal decomposition. Due to these distinctive characteristics, CNTs are good supporting materials which can support a high dispersion of Pt nanoparticles due to their large surface area and particular morphology. In addition, the metal particles supported on the CNTs seemed to be less susceptible to CO poisoning than the traditional catalyst systems (Hamon et al. 1999). As a result, Pt nanoparticle-decorated carbon nanotubes are of significant interest among the researches in the area of electrocatalysis.

An increased attention has been paid on the composite of conducting polymers with carbon that was taken as catalyst supports. The introduction of the conducting polymer to electrocatalysts helps increasing the interfacial properties between the electrode and electrolyte. Composite materials based on the combination of conducting polymer and CNT have shown properties of the individual components with synergistic effect (Riggs et al. 2000; Santhosh et al. 2006; Wu et al. 2006). Wu et al. (2005) and Liu et al. (2008) synthesized PANI-XC-72 carbon black, PANI-SWNTs composite membrane by electrochemical method and used them as Pt and Pt–Ru catalyst supports for methanol oxidation. The results indicated that the composite supports could improve the dispersion of the catalysts with excellent catalytic activity. Santhosh et al. (2006) prepared gold nanoparticles onto a PANI-grafted-MWNT (MWNT-g-PANI)-based catalyst through a two-step electrochemical process. The results indicate that the Au/MWNT-g-PANI catalyst showed good catalytic current for oxidation of methanol.

In view of this regard, this work is aimed in exploring the activity of polyaniline and carbon nanotubes towards the oxidation of methanol. This is a continuation of our previous studies on electrooxidation of organic molecules using various supporting materials (Selvaraj et al. 2009; Nirmala Grace and Pandian 2006). The present investigation describes a simple route for the spontaneous formation of Pt nanoparticles on surface-oxidized multi-walled carbon nanotubes (MWCNT) sidewalls using ethylene glycol as reducing agent. The prepared nanoparticles are characterized using analytical techniques such as TEM, FT-IR spectroscopy and XRD. The prepared Pt-MWCNT catalysts were utilized for investigating the electrooxidation of methanol.

Experimental procedure

Materials

The electrocatalyst precursor salt $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was purchased from Sigma-Aldrich. MWCNT obtained from Aldrich (diameter 10–50 nm, length 0.1–10 μm , AS >90%)

were rinsed with double-distilled water and dried. Solvents such as nitric acid, HCl, ethylene glycol (EG), KOH, acetone and methanol were used as received from local suppliers. All chemicals were of reagent grade and double-distilled water was used throughout the experiments. All experiments were carried out at 25°C.

Equipment and methods

The size of the particles is confirmed using HR-TEM (JEOL) with an accelerating voltage of 120 kV. Samples for TEM analysis were prepared by dispersing the catalyst in double-distilled water, transferring a drop of this suspension onto a colloidal coated copper grid, and subsequently drying in air. X-ray diffraction (XRD) patterns were obtained with a BRUKER, D8 advance generator and diffractometer using $\text{CuK}\alpha$ radiation and a graphite monochromator.

Pretreatment of MWCNT

Required amount of MWCNT was centrifuged in the presence of conc. HCl. The precipitate was filtered, washed with acetone, Millipore water and dried under vacuum for 60°C in a hot air oven overnight. After the purification process, the surface oxidation of the MWCNT was carried out by refluxing MWCNT in 25 mL of conc. HNO_3 at 120°C for 24 h to remove impurities and to generate surface functional groups. Finally, the treated MWCNT was diluted with water, filtered, washed with excess distilled water and dried at 60°C in vacuum overnight. After the oxidation treatment, a surface-oxidized MWCNT sample is obtained.

Microwave synthesis of Pt-MWCNT

Pt-MWCNT catalyst was prepared by microwave heating of an ethylene glycolic (EG) solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. A typical preparation consists of the following steps: to a 25 mL of ethylene glycol, 80 mg of functionalized MWCNT was added under sonication. The sample was sonicated till all the MWCNTs are completely dispersed in solvent. Then, 4.0 mL of 0.05 M H_2PtCl_6 was added to the solution. Immediately, a black suspension was obtained; 0.8 mL of 0.04 M KOH was added slowly in drops to the above black suspension. The beaker was then placed in a household microwave oven and then heated for 120 s under a microwave power of 1,000 W (SANYO EM-S1563, 2,450 MHz, 800 W), the point at which Pt particles were reduced from the solution. The as-prepared suspension was filtered, and the residue was washed three times with acetone and Millipore (18.2 M Ω /cm) water. The product was dried under vacuum at 60°C.

Electrochemical measurements

All the electrochemical experiments were performed on a CHI 600C application CH Instruments Electrochemical Workstation. A three-electrode system was employed with an Ag/AgCl as the reference electrode, a platinum wire as the counter electrode, and a platinum disk (with an area of 0.0314 cm²) as the working electrode. The electrochemical properties of the Pt-MWCNT electrode was investigated in 0.5 M CH_3OH + 0.5 M H_2SO_4 by cyclic voltammetry in the range of -0.2 to $+1.2$ V at a sweep rate of 50 mVs⁻¹. All measurements were carried out at room temperature. The platinum (Pt)-catalyst electrode was prepared by the following procedure: (1) the platinum working electrode (surface) was washed with Millipore water and acetone, (2) the catalyst solution was made by sonicating 2 mg catalyst in 1 mL of ethanol and (3) 10 μL of 2 mg/mL catalyst solution was added to the surface of the Pt electrode and dried in air to get Pt_{disk}/Pt-MWCNT and to get Pt_{disk}/PANI/Pt-MWCNT, the catalyst was added to the monomer solution of polyaniline and further electropolymerized.

Electrochemical deposition of Pt-MWCNT/PANI on working electrode

Polyaniline (PANI) is deposited electrochemically over the working Pt electrode in 0.5 M H_2SO_4 and 0.1 M aniline in a potential range of -0.2 to $+1.0$ V at 0.05 V/s scan rate for 25 consecutive cycles to get Pt_{disk}/PANI electrode. For incorporation of the catalyst within the growing polymer matrix, 2 mg/mL of the synthesized Pt-MWCNT catalyst was added to 10 cm³ of 0.1 M aniline in 0.5 M H_2SO_4 . The resultant solution was cycled between -0.2 and 1.0 V versus Ag/AgCl at 0.05 V/s to generate Pt_{disk}/PANI/Pt-MWCNT electrode. Similarly, other catalyst-based electrodes such as Pt_{disk}/PANI, Pt_{disk}/MWCNT, Pt_{disk}/Pt-MWCNT and Pt_{disk}/PANI-MWCNT were prepared in a similar way. In the case of Pt_{disk}/MWCNT- and Pt_{disk}/PANI-MWCNT-based electrodes, required amount of functionalized MWCNT instead of Pt-MWCNT is added to the aniline solution and further electropolymerized as explained previously.

Experimental results

UV–vis spectral results

A UV was recorded for the catalyst to ensure that Pt ions are reduced to Pt nanoparticles. As seen Fig. 1, a peak at 270 nm for PtCl_6^{2-} was observed, which is due to ligand-to-metal charge transfer transitions of Pt ions (Fig. 1a). After microwave reduction, the Pt-MWCNT catalysts was washed and finally isolated. From the UV analysis of the final prepared

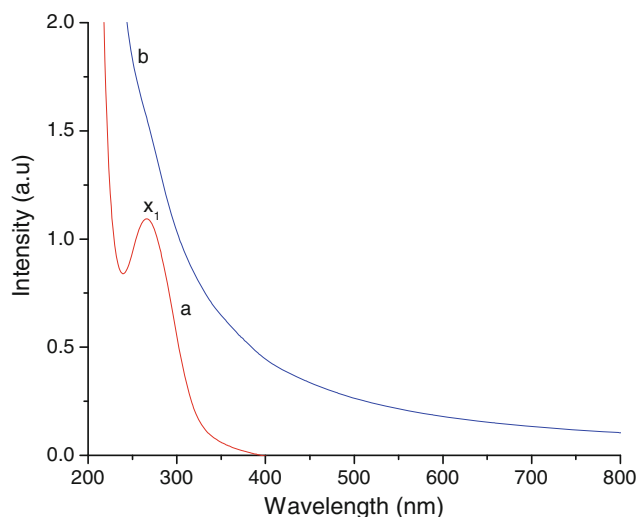


Fig. 1 UV-visible spectrum of Pt-MWCNT recorded before (a) and after (b) microwave reduction (where x_1 represents the initial absorptions of Pt metal ions before reduction)

catalysts, the peak disappeared and the solution was black in color. A weak tail stretching across 200–800 nm was finally observed which is characteristic of Pt nanoparticles.

Spectral evolution of CNTs

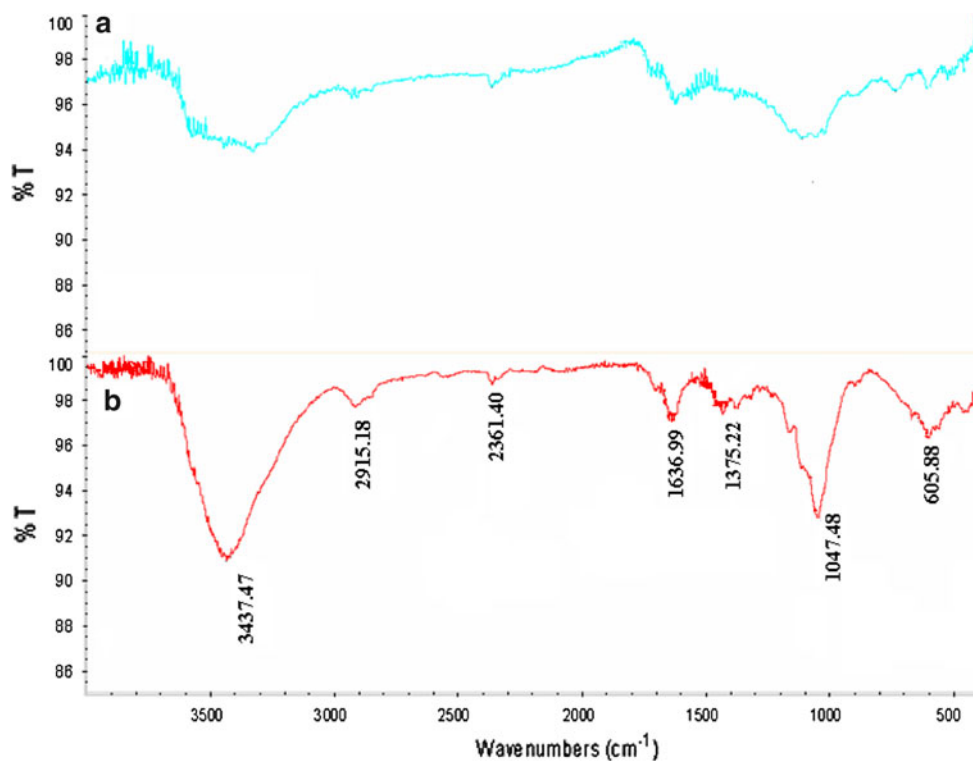
It is well documented that a stronger nitric acid solution generates more functional groups on CNT surfaces than a

weaker one resulting in better electrocatalyst formation and hence conc. HNO_3 is used to generate more functional groups on carbon nanotubes (Han et al. 2004). Examination on surfaces of acid-oxidized carbon nanotubes is carried out using a Fourier transform infrared (FT-IR) spectrophotometer to ensure the formation of desired functional groups. It is clear that several types of functional groups, particularly carbonyl and hydroxyl groups have been generated on acid-oxidized carbon nanotube surfaces. Figure 2 shows the IR spectrum of unfunctionalized and functionalized MWCNTs, respectively. As seen from the spectrum of functionalized MWCNTs, the presence of bands at 1,636 and 3,434 cm^{-1} confirmed the presence of carbonyl and hydroxyl moieties of carboxylic acid group. This confirms that the carbon nanotubes has been well functionalized with $-\text{COOH}$, which is absent in unfunctionalized CNTs (Fig. 2a). The presence of $-\text{COOH}$ groups on the surface of the MWCNTs is advantageous for a better deposition of metal particles on the surface of the CNTs (Fig. 2b). It is reported that the dominant functional group is carboxylic group generated by strong acid treatment (Han et al. 2004).

Microstructural characterization

The electrocatalyst comprising purified carbon nanotubes modified with Pt nanoparticles is characterized by TEM analysis to observe the CNT surfaces. The surface morphology was found to be uniform and tubular walls are

Fig. 2 FT-IR spectrum of (a) unfunctionalized and (b) functionalized multi-walled carbon nanotubes



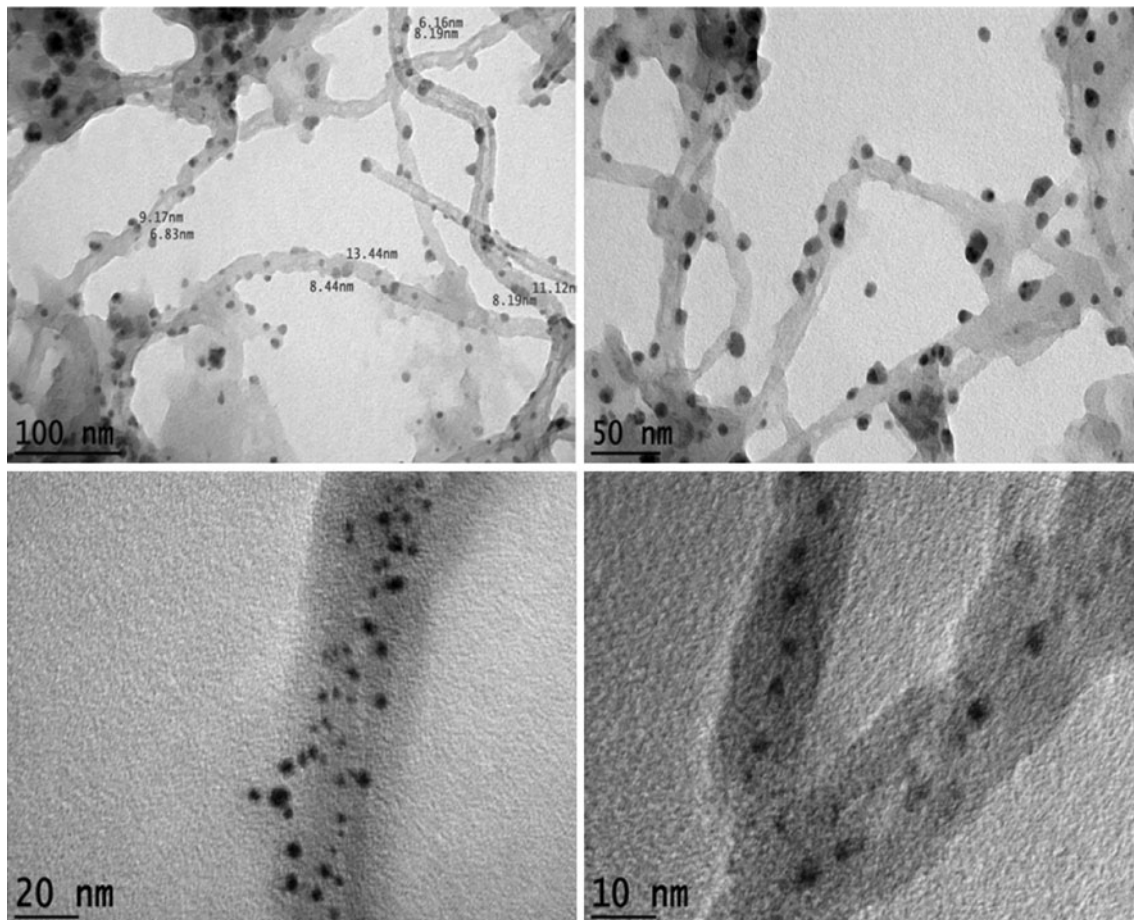


Fig. 3 TEM micrographs of Pt-MWCNT catalysts at various magnifications

sufficiently decorated with nanoparticles as seen from the TEM images (Fig. 3). Pt-MWCNT composites have three-dimensional porous structure. It can be seen that the nanotubes are well separated from each other (Fig. 3), which can be due to an attainment of hydrophilic properties of the nanotubes offered by the high-density surface functional groups formed on the outer walls of the MWCNTs during the acid treatment. From the TEM image, the Pt particle size is around 10–15 nm. The microwave-assisted heating method had evidently facilitated the formation of smaller and more uniform metal particles. It is generally agreed that the size of metal nanoparticles is determined by the rate of reduction of the metal precursor. The dielectric constant (41.4 at 298 K) and the dielectric loss of ethylene glycol are high, and hence rapid heating occurs easily under microwave irradiation (Colmenares et al. 2006). Fast heating rates can accelerate the formation of the metal nanoparticles, and the uniform microwave irradiation provides more homogeneous circumstances for their nucleation and growth.

XRD analysis

Figure 4 shows the XRD pattern of Pt-MWCNT catalysts. The diffraction peaks at about 40° , 46.5° , 68.7° , and 79.5° are due to the Pt (111), (200), (220) and (311) reflections, respectively, which represents the typical character of crystalline face-centered cubic (fcc) phase and a peak corresponding to (002) graphitized CNTs could also be seen. There are no other distinct reflection peaks.

Electrochemical performance of Pt-MWCNT and Pt-MWCNT/PANI

The electrochemical surface area of Pt particles is an important concern and the large electrochemical surface area is always desirable in view of the fact that the catalytic reactions often occur on the surface of the catalyst. The real surface of Pt-based catalysts could be estimated from the integrated charge of the hydrogen absorption region of the CV in 0.5 M H_2SO_4 (Fig. 5a). The electrochemical active

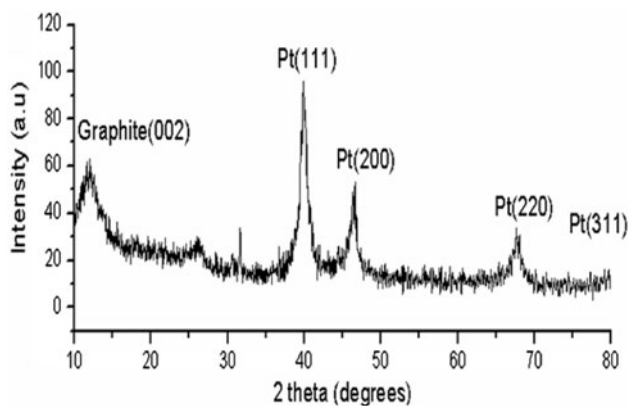


Fig. 4 XRD patterns of Pt-MWCNT catalyst

surface areas of different catalysts were calculated according to the following formula (Wang et al. 2010; Li et al. 2005):

$$A_{EL} (\text{m}^2 \text{g}^{-1} \text{Pt}) = \frac{Q_H}{0.21 \times 10^{-3} C \times g_{Pt}},$$

where A_{EL} is the Pt surface obtained electrochemically, Q_H is the amount of charge exchanged during the electro-sorption of hydrogen atoms onto the Pt surface. The areas in m^2 were calculated from the above formula assuming a correspondence value of 0.21 mC (calculated from the surface density of 1.3×10^{15} atom per cm^2 , a value generally admitted for polycrystalline Pt electrodes) (Ralph et al. 1997) and the Pt loading. The electrochemical active surface areas of catalysts are shown in Table 1. It can be seen that the area of hydrogen adsorption and desorption peak for the $\text{Pt}_{\text{disk}}/\text{PANI}/\text{Pt-MWCNT}$ electrode is much bigger than that of the $\text{Pt}_{\text{disk}}/\text{Pt-MWCNT}$ electrode, which

means that the former catalyst-based electrode has a relative larger active surface area.

To investigate the effects of MWCNT on the electrocatalytic activities of the catalyst, the catalytic properties of the as-prepared catalysts towards the methanol oxidation reaction were characterized by cyclic voltammetry (CV) in 0.5 M $\text{H}_2\text{SO}_4 + 0.5$ M CH_3OH solution. The electrocatalytic activities of the catalysts towards methanol oxidation for Bare Pt_{disk} , $\text{Pt}_{\text{disk}}/\text{PANI}$, $\text{Pt}_{\text{disk}}/\text{MWCNT}$, $\text{Pt}_{\text{disk}}/\text{Pt-MWCNT}$, $\text{Pt}_{\text{disk}}/\text{PANI-MWCNT}$, $\text{Pt}_{\text{disk}}/\text{PANI}/\text{Pt-MWCNT}$ measured by cyclic voltammetry at a potential scan rate of 50 mVs^{-1} are shown in Fig. 5b. The methanol oxidation activity could be reflected by the magnitude of the anodic peak current in the forward scan. The CV starts from open circuit potential and sweep within the entire potential region between -0.2 and 1.0 V versus Ag/AgCl. As shown in the CV curves, there are two oxidation peaks, related to the oxidation processes of methanol and the corresponding intermediates produced during the methanol oxidation. It is clear that the electrocatalytic activity of Pt-MWCNT/PANI catalyst is higher than that of Pt-MWCNT and other catalysts. The Pt-MWCNT/PANI sample exhibits the electrochemical activities that resulted from a typical redox response. Redox peaks at around 0.2 and 0.7 V serve for the conversion of leucoemeraldine to emeraldine, and emeraldine to pernigraniline, respectively. As can be observed in the figure, the PANI/CNT system is superior in the aspect of higher current. This higher current stands for the higher effective surface area that is accessible to electrolytes. The electrocatalytic activity for Pt-MWCNT and PANI-MWCNT on Pt disk electrodes is almost comparable. The forward oxidation peak current is slightly

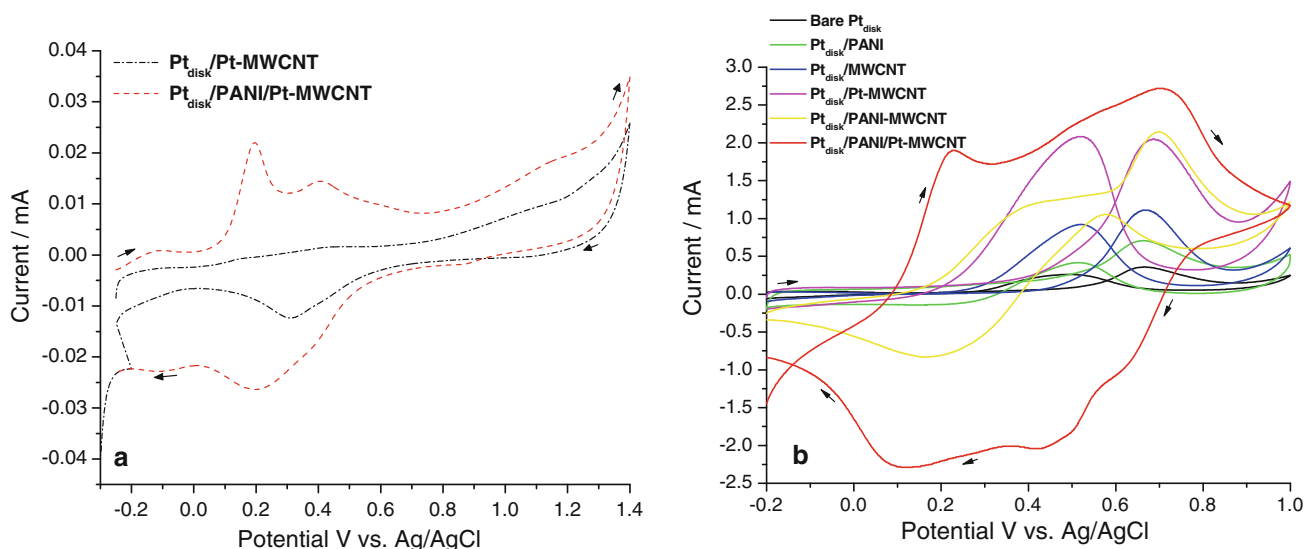


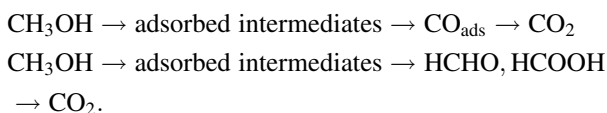
Fig. 5 a Cyclic voltammograms of the prepared catalyst modified electrodes in a 0.5 M H_2SO_4 , b 0.5 M $\text{H}_2\text{SO}_4 + 0.5$ M CH_3OH solution at a scan rate of 50 mVs^{-1}

Table 1 Real (active) surface areas of Pt_{disk}/Pt-MWCNT and Pt_{disk}/PANI/Pt-MWCNT catalysts as determined by hydrogen electroadsorption

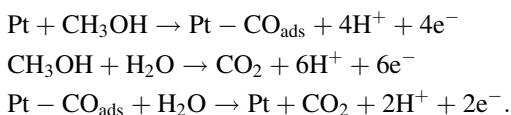
Catalysts	Catalyst loading (mg)	Q_H (mC)	A_{EL} (m ² /g)
Pt _{disk} /Pt-MWCNT	0.02	1.45	34.52
Pt _{disk} /PANI/Pt-MWCNT	0.02	2.17	58.88

Q_H : charges exchanged during the electroadsorption of hydrogen, A_{EL} : real surface area obtained electrochemically per gram of catalyst

higher for MWCNT-PANI catalysts but the backward oxidation current was greater for Pt-MWCNT catalyst. The forward scan is attributed to methanol oxidation, forming Pt adsorbed carbonaceous intermediates, including CO and CO₂. This adsorbed CO causes loss of activity of the electrocatalyst. The total oxidation process of methanol consists of a pattern of parallel reactions which can be formulated as follows (Lordi et al. 2001):



Among CH₃OH, HCHO and HCOOH, methanol is the least reactive. Thus, in the stepwise oxidation of CH₃OH to CO₂, the first 2e⁻ oxidation step, i.e., the conversion of methanol to formaldehyde is the rate determining step. The elementary step which determines the rate might be either C–H bond breaking or C–O bond formation. Studies on bare Pt have shown that the methanol oxidation reaction is inhibited by the formation of poison, identified as a –CO or a –COH species. The –COH species have been suggested to be a detectable intermediate in the formation of –CO on Pt (Arenz et al. 2005). The general steps of methanol oxidation are shown below:



The backward oxidation peak (final equation) is attributed to the additional oxidation of the adsorbed carbonaceous species to CO₂. As shown in the figure, the onset and peak potentials of methanol oxidation reaction are observed at 0.38 and 0.7 V, respectively, in the forward scan, which corresponds to the methanol oxidation, while in the reverse scan, the adsorbed intermediates produce another oxidation peak at around 0.45 V. In principle, the onset potential is related to the breaking of C–H bonds and subsequent removal of the C intermediates by oxidizing them with OH_{ads}. From the graph, it can be seen that the onset potential is lower for Pt-MWCNT/PANI catalyst compared to the other catalysts. A lesser onset potential

with a higher current is the characteristics of a good catalyst. These voltammogram results demonstrated that the Pt-MWCNT/PANI nanocatalysts are efficient for methanol oxidation reaction activity and enhancing the tolerance towards poisoning at the electrode surface. In this paper, a good catalytic current was observed without the need of alloying with other metals using appropriate support materials viz. polyaniline and carbon nanotubes.

Effect of scan rate and methanol concentration on electrocatalytic property of Pt-MWCNT/PANI-modified electrodes

A further investigation was done to know about the transport characteristics of methanol in Pt-MWCNT/PANI-modified electrodes. The results presented here are for the Pt-MWCNT/PANI-decorated platinum working electrode, since this modified electrode exhibits the highest activity. From Fig. 6a, it can be seen that the peak currents of methanol oxidation increased with the increase of scan rates. For the methanol oxidation at Pt_{disk}/PANI/Pt-MWCNT electrode, a linear relationship between the peak current density (i_p) obtained from the forward CV scans and square root of the scan rate ($v^{1/2}$) is obtained as shown in Fig. 6b. This suggests that the oxidation of methanol at Pt_{disk}/PANI/Pt-MWCNT electrode is controlled by diffusion process of methanol.

The further proof is obtained from the relationship between the peak current density and methanol concentration, which is shown in Fig. 7a. From the figure, the peak current density (i_p) increases with an increase of the methanol concentration. It was clearly observed that the oxidation current density increases with increasing methanol concentration and starts decreasing after 5 M. It seems that this effect is due to the saturation of active sites at the surface of the electrode. In accordance with this result, the maximum concentration of methanol to obtain a higher current density using Pt-MWCNT/PANI catalyst is considered as about 5 M.

The long-term cycle stability of Pt-MWCNT/PANI-modified electrode

In practical application, the long-term cycle stability of electrocatalysts is very important. In this work, the long-term cycle stability of Pt-MWCNT/PANI has been evaluated by cyclic voltammetry in 0.5 M CH₃OH + 0.5 M H₂SO₄ aqueous solution. The corresponding results are shown in Fig. 7b. From the figure, it can be observed that the peak current density of methanol oxidation obtained from forward CV sweep decreases gradually with the increase of the cycle number. At the 600th cycle the peak current density is reduced compared to the first cycle. This

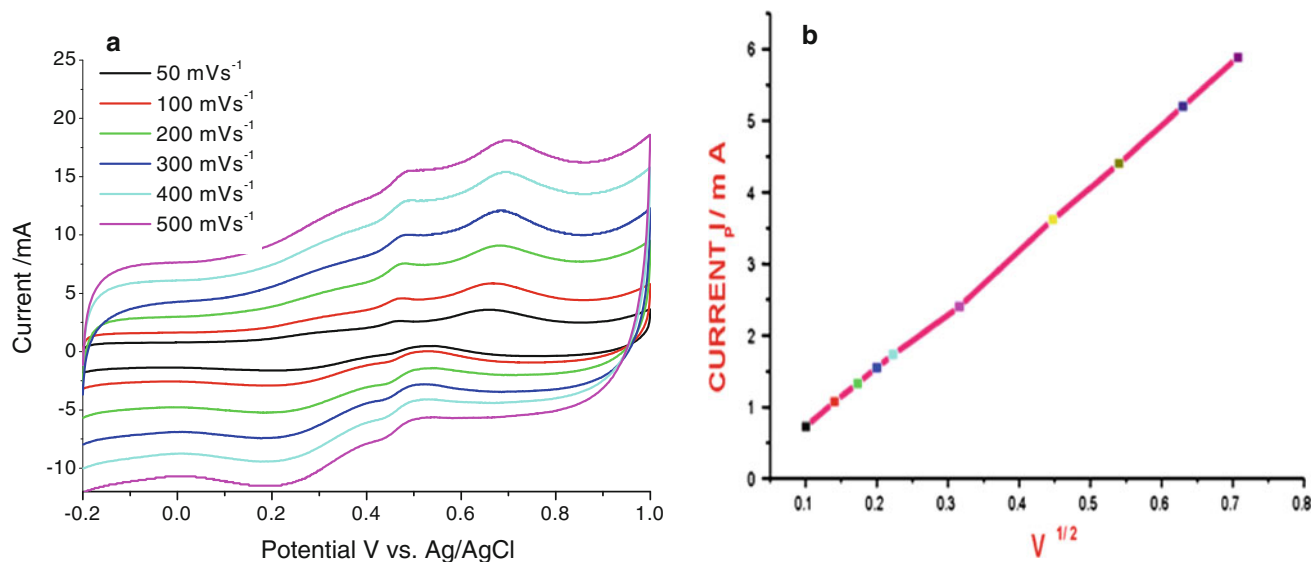


Fig. 6 **a** Effect of scan rate on methanol oxidation using Pt-MWCNT/PANI in 0.5 M H₂SO₄ + 0.5 M CH₃OH solution, **b** variation of the peak current density i_p of methanol oxidation obtained

from the forward scan with $v^{1/2}$ in 0.5 M CH₃OH + 0.5 M H₂SO₄ aqueous solutions at a scan rate of 50 mVs⁻¹

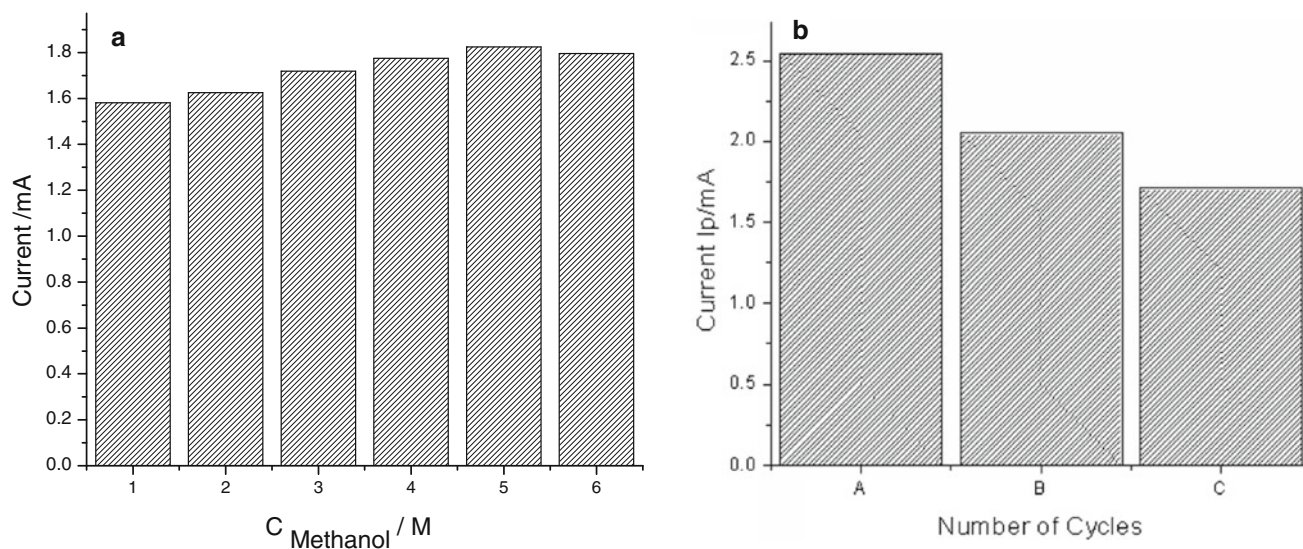


Fig. 7 **a** Dependence of the peak current density obtained from the forward CV scan upon methanol concentration of 0.5, 1, 2, 3, 4, 5, 6 M. Scan rate, 50 mVs⁻¹. **b** The recovery ability of catalyst after 600 continuous cycles. *Column A* the first cycle, *column B* the 600th

cycle, *column C* the 601st cycle in freshly prepared 0.5 M CH₃OH + 0.5 M H₂SO₄ aqueous solution; scan rate of CV 50 mVs⁻¹

may result from three reasons: accumulation of poisonous species (such as CO_{ads}) on the surface of the nanoparticles, change of the surface structure of the Pt-MWCNT/PANI catalyst and methanol consumption during the successive scans. For the third reason, the catalyst was investigated again by CV in freshly prepared 0.5 M CH₃OH + 0.5 M H₂SO₄ aqueous solution and the peak current density was obtained to be 1.7 mA, which was nearly 70% of that at the first cycle (Fig. 7b). This suggests that the main reason for the decrease of current density in the continuous 600 cycles

may be the consumption of methanol. In the case of other catalysts like Pt_{disk}/PANI, Pt_{disk}/MWCNT, Pt_{disk}/Pt-MWCNT, and Pt_{disk}/PANI-MWCNT, the current for the 600th cycle decreased more compared to Pt_{disk}/PANI/Pt-MWCNT catalyst. In the latter, at the 600th cycle, the current for nearly 80% of the first cycle. In the case of other catalysts, the order is as follows: Pt_{disk}/PANI (61%), Pt_{disk}/MWCNT (67%), Pt_{disk}/Pt-MWCNT (70%), and Pt_{disk}/PANI-MWCNT (75%). From these results, it can be seen that Pt_{disk}/PANI/Pt-MWCNT catalyst has better long-term

stability than with the other catalysts. The excellent long-term cycle stability of the Pt-MWCNT/PANI catalyst is a good alternative catalyst in DMFC.

Conclusion

Pt nanoparticles on multiwall carbon nanotubes have been successfully synthesized using microwave heating technique. The synthesized catalyst materials were well-distributed with a small particle size of 10–15 nm. The electrocatalytic activity of Pt-MWCNT/PANI catalyst is higher than that of Pt-MWCNT and Pt nanoparticles suggesting that a combination of CNT and polyaniline enhances the electrocatalytic property. The nanotubular materials act as conducting material that improves electron transfer between catalyst particles and nanotubes and also act as accessible mesoporous network for catalytic particles. Such kind of catalysts could be used for practical DMFC applications.

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References

- Antolinia E (2010) Composite materials: an emerging class of fuel cell catalyst supports. *Appl Catal B Environ* 100:413–426
- Appleby AJ, Foulkes RB (1989) Fuel cell handbook. Van Nostrand Reinhold, New York
- Arenz M, Stamenkovic V, Bliznac BB, Mayrhofer KJ, Markovic NM, Ross PN (2005) Carbon-supported Pt–Sn electrocatalysts for the anodic oxidation of H₂, CO, and H₂/CO mixtures. Part II. The structure-activity relationship. *J Catal* 232:402–410
- Arico AS, Srinivasan S, Antonucci V (2001) DMFCs: from fundamental aspects to technology development. *Fuel cells* 1:133–161
- Bouzek K, Mangold KM, Juttner K (2000) Platinum distribution and electrocatalytic properties of modified polypyrrole films. *Electrochim Acta* 46:661–670
- Chen Z, Xu L, Li W, Waje M, Yan Y (2006) Polyaniline nanofibre supported platinum nanoelectrocatalysts for direct methanol fuel cells. *Nanotechnology* 17:5254–5259
- Chen S, Ye F, Lin W (2009) Carbon nanotubes-Nafion composites as Pt–Ru catalyst support for methanol electro-oxidation in acid media. *J Nat Gas Chem* 18:199–204
- Chu D, Jiang R (2002) Novel electrocatalysts for direct methanol fuel cells. *Solid State Ionics* 148:591–599
- Colmenares L, Wang H, Jusys Z, Jiang L, Yan S, Sun GQ (2006) Ethanol oxidation on novel, carbon supported Pt alloy catalysts—model studies under defined diffusion conditions. *Electrochim Acta* 52:221–233
- Gomez R, Weaver MJ (1997) Electrochemical infrared studies of monocrystalline iridium surfaces part I: electrooxidation of formic acid and methanol. *J Electroanal Chem* 435:205–215
- Guo DJ, Li HL (2004) High dispersion and electrocatalytic properties of Pt nanoparticles on SWNT bundles. *J Electroanal Chem* 573:197–202
- Guo S, Dong S, Wang E (2009) Polyaniline/Pt hybrid nanofibers: high-efficiency nanoelectrocatalysts for electrochemical devices. *Small* 5:1869–1876
- Habibi B, Pournaghi-Azar MH (2010) Methanol oxidation on the polymer coated and polymer-stabilized Pt nano-particles: a comparative study of permeability and catalyst particle distribution ability of the PANI and its derivatives. *Int J Hydrogen Energy* 35:9318–9328
- Hamon MA, Chen J, Hu H, Chen Y, Itkis ME, Rao AM, Eklund PC, Haddon RC (1999) Dissolution of single-walled carbon nanotubes. *Adv Mater* 11:834–840
- Han KI, Lee JS, Park SO, Lee SW, Park YW, Kim H (2004) Studies on the anode catalysts of carbon nanotube for DMFC. *Electrochim Acta* 50:791–794
- He Z, Chen J, Liu D, Tang H, Deng W, Kuang Y (2004a) Deposition and electrocatalytic properties of platinum nanoparticles on carbon nanotubes for methanol electrooxidation. *Mater Chem Phys* 85:396–401
- He Z, Chen J, Liu D, Zhou H, Kuang Y (2004b) Electrodeposition of Pt–Ru nanoparticles on carbon nanotubes and their electrocatalytic properties for methanol electrooxidation. *Diam Relat Mater* 13:1764–1770
- Hoa LQ, Sugano Y, Yoshikawa H, Saito M, Tamiya E (2011) Structural assembly effects of Pt nanoparticle-carbon nanotube-polyaniline nanocomposites on the enhancement of biohydrogen fuel cell performance. *Electrochimica Acta* 56:9875–9882
- Huang YF, Lin CW, Chang CS, Ho MJ (2011) Alternative platinum electrocatalyst supporter with micro/nanostructured polyaniline for direct methanol fuel cell applications. *Electrochim Acta* 56:5679–5685
- Ishikawa Y, Liao MS, Cabrera CR (2000) Oxidation of methanol on platinum, ruthenium and mixed Pt–M metals (M= Ru, Sn): a theoretical study. *Surf Sci* 463:66–80
- Kristian N, Yu Y, Gunawan P, Xu R, Deng W, Liu X, Wang X (2009) Controlled synthesis of Pt-decorated Au nanostructure and its promoted activity toward formic acid electro-oxidation. *Electrochimica Acta* 54:4916–4924
- Lamy C, Leger JM, Garnier F (1997) Handbook of organic conductive molecules and polymers. In: Nalwa HS (ed) *Conductive polymers: spectroscopy and physical properties*, vol 471, 3rd edn. Wiley, NY
- Lamy C, Lima A, LeRhun V, Delime F, Coutanceau C, Leger FM (2002) Recent advances in the development of direct alcohol fuel cells (DAFC). *J Power Sour* 105:283–296
- Leger JM, Lamy C (1990) The direct oxidation of methanol at platinum based catalytic electrodes: what is new since ten years? *Ber Bunsenges Phys Chem* 94:1021–1025
- Li X, Chen WX, Zhao J, Xing W, Xu ZD (2005) Microwave polyol synthesis of Pt/CNTs catalysts: effects of pH on particle size and electrocatalytic activity for methanol electrooxidation. *Carbon* 43:2168–2174
- Lim DH, Lee WD, Lee HI (2008) Highly dispersed and nano-sized Pt based electrocatalysts for low-temperature fuel cells. *Catal Surv Asia* 12:310–325
- Liu Z, Lin X, Lee JY, Zhang W, Han M, Gan LM (2002) Preparation and characterization of platinum-based electrocatalysts on multiwalled carbon nanotubes for proton exchange membrane fuel cells. *Langmuir* 18:4054–4060
- Liu H, Song C, Zhang L, Zhang J, Wang H, Wilkinson DP (2006) A review of anode catalysis in the direct methanol fuel cell. *J Power Sour* 155:95–110
- Liu FJ, Huang LM, Wen TC, Li CF, Huang SL, Gopalan A (2008) Platinum particles dispersed polyaniline-modified electrodes containing sulfonated polyelectrolyte for methanol oxidation. *Synth Metals* 158:767–774
- Lordi V, Yao N, Wei J (2001) Method for supporting platinum on single-walled carbon nanotubes for a selective hydrogenation catalyst. *Chem Mater* 13:733–737

- Nirmala Grace A, Pandian K (2006) Pt, Pt–Pd and Pt–Pd/Ru nanoparticles entrapped polyaniline electrodes—a potent electrocatalyst towards the oxidation of glycerol. *Electrochem Commun* 8:1340–1348
- Parsons R, Vandernoof T (1988) The oxidation of small organic molecules: a survey of recent fuel cell related research. *J Electroanal Chem* 257:9–45
- Qu B, Xu YT, Lin SJ, Zheng YF, Dai LZ (2010) Fabrication of Pt nanoparticles decorated Ppy-MWNTs composites and their electrocatalytic activity for methanol oxidation. *Synth Metals* 160:732–742
- Rajesh B, Karthik V, Karthikeyan S, Thampi KR, Bonard JM, Viswanathan B (2002) Pt-WO₃ supported on carbon nanotubes as possible anodes for direct methanol fuel cells. *Fuel* 81:2177
- Ralph TR, Hards GA, Keating SA, Campbell DP, Wilkinson M, Davis J, St-pierre MC, Johnson J (1997) *Electrochem Soc* 144:3845–3857
- Ren XM, Zelenay P, Thomas S, Davey J, Gottesfeld S (2000) Recent advances in direct methanol fuel cells at Los Alamos National Laboratory. *J Power Sources* 86:111–116
- Riggs JE, Guo Z, Carroll DL, Sun YP (2000) Strong luminescence of solubilized carbon nanotubes. *J Am Chem Soc* 122:5879–5880
- Santhosh P, Gopalan A, Lee KP (2006) Gold nanoparticles dispersed polyaniline grafted multiwall carbon nanotubes as newer electrocatalysts: preparation and performances for methanol oxidation. *J Catal* 238:177–185
- Selvaraj V, Nirmala Grace A, Alagar M (2009) Electrocatalytic oxidation of formic acid and formaldehyde on nanoparticle decorated single walled carbon nanotubes. *J Colloid Interface Sci* 333:254–262
- Uchida M, Aoyama Y, Tanabe N, Yanagihara N, Eda N, Ohta A (1995) Influences of both carbon supports and heat-treatment of supported catalyst on electrochemical oxidation of methanol. *J Electrochem Soc* 142:2572–2576
- Wang Y, Sheng ZM, Yang H, Jiang SP, Li CM (2010a) Electrocatalysis of carbon black or activated carbon nanotubes-supported Pd–Ag towards methanol oxidation in alkaline media. *Int J Hydrogen Energy* 35:10087–10093
- Wang RF, Li H, Ji S, Wang H, Lei ZQ (2010b) Pt decorating of PdNi/C as electrocatalysts for oxygen reduction. *Electrochim Acta* 55:1519–1522
- Wu G, Li L, Li JH, Xu BQ (2005) Polyaniline-carbon composite films as supports of Pt and PtRu particles for methanol electrooxidation. *Carbon* 43:2579–2587
- Wu G, Li L, Li J-H, Xu B-Q (2006) Methanol electrooxidation on Pt particles dispersed into PANI/SWNT composite films. *J Power Sour* 155:118–127
- Zhao Y, Yang X, Tian J, Wang F, Zhan L (2010) Methanol electrooxidation on Ni–Pd core-shell nanoparticles supported on multi-walled carbon nanotubes in alkaline media. *Int J Hydrogen Energy* 35:3249–3257
- Zhiani M, Rezaei B, Jalili J (2010) Methanol electro-oxidation on Pt/C modified by polyaniline nanofibers for DMFC applications. *Int J Hydrogen Energy* 35:9298–9305
- Zhou ZH, Li WS, Fu Z, Xiang XD (2010) Carbon nanotube-supported Pt-HxMoO₃ as electrocatalyst for methanol oxidation. *Int J Hydrogen Energy* 35:936–941