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Modification of multi-walled carbon nanotubes by microwave digestion method as electrocatalyst supports for direct methanol fuel cell applications

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Abstract

Multi-walled carbon nanotubes (MWCNTs) which were directly synthesized on carbon cloth were modified by a microwave digestion method in 5 M HNO_3 for supporting Pt nanoparticles. The characterizations of modified CNTs were carried out by TEM, XPS, FTIR and Raman spectroscopy. The HRTEM image shows the caps of MWCNTs are opened after modifying by microwave digestion method. The open-end and undamaged MWCNTs can provide a larger surface area for supporting more catalysts. Furthermore, the methanol electrocatalytic oxidation of microwave digestion treated Pt/MWCNTs electrode shows higher current density than pristine and nitric acid-treated MWCNTs from cyclic voltammograms. This can be an effective and undamaged method for modifying CNTs.

Keywords: Multi-walled carbon nanotubes; Microwave digestion; Direct methanol fuel cell; Catalyst supports; Polyol method

1. Introduction

In the past decades, carbon nanotubes (CNTs) are widely applied in many fields for their high surface area, high electrical conductivity, good chemical stability and significant mechanical strength [1]. Due to the high surface areas of its outside walls and central hollow structure; CNTs can be used as catalyst supports and gas storage media for a variety of applications in fuel cell [2–5]. Precious metals, such as Pt and Ru, are dispersed on carbon nanotubes and resulting materials for DMFC applications showed good electrocatalytic behaviors [6–8]. Unfortunately, the surface of pristine CNT is chemically inert and hydrophobic, which is unfavorable for supporting catalyst. Therefore, the modification of the surface of CNT with functional groups is essential for further applications. Nitric acid which is a strong oxidant is commonly used for functionalizing the CNT surface. Generally, electrocatalysts which supported on functionalized CNTs are synthesized by two steps. Raw CNTs were first refluxed with nitric acid and then metal precursors attached to functionalized CNTs surfaces [9]. The step of refluxing CNTs in nitric acid not only opens the caps of CNTs, but functionalizes the surfaces of CNTs with carboxylic groups. However, conventional nitric acid treatments for modifying CNTs usually need to reflux CNTs for a long time and sometimes damage the structures of CNTs seriously.

Here, we report an efficient and mild method using microwave digestion system for modifying CNTs in a short time, which could be widely used in modification or purification of CNTs for fuel cell applications.

2. Experimental

2.1. Modifications of MWCNTs

Multi-walled carbon nanotubes were directly synthesized on the iron deposited carbon cloth (MWCNTs/CC)

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by bias assisted microwave plasma enhanced chemical vapor deposition system. The details of synthesis processes of MWCNTs are described in our previous work [10]. After that, MWCNTs were modified utilizing a conventional nitric acid-treatment and a microwave digestion method. The MWCNTs immersed in 14 M HNO_3 solution and refluxed at 80 °C for 18 h. And then, the sample was filtered with 0.1 mm PTFE (poly-(tetrafluoroethylene)) membrane in deionized water as the conventional part. On the other hand, an alternative acidic treatment in microwave digestion system (Milestone Microwave Labstation ETHOSD) was used to modify MWCNTs. 1 cm^2 of MWCNTs/CC was placed in a 100 ml Pyrex digestion tube. The first digestion step was to heat the system from room temperature to 210 °C within 20 min with 5 M HNO_3. The microwave power was set at 100 W. The second digestion step was to keep the temperature at 210 °C for 30 min. After digestion; the sample was also filtered with 0.1 mm PTFE membrane in deionized water. The total modification time by microwave digestion method was less than 1 h. More information of the microwave digestion method can be found in our previous works [11–13].

2.2. Preparation and Dispersion of Pt nanoparticles on MWCNTs/CC

The Pt nanoparticles were synthesized by the polyol processes and then dispersed on MWCNTs/CC sample. Initial materials included metallic complex salts of $H_2PtCl_6 \cdot 6H_2O$ (SHOWA, 98 wt%), polymer protector agent PVP-40 [MW ~38 000–40 000, poly(vinyl pyrrolidone)) (Sigma, 99 wt%)], and the solvent Ethylene Glycol (E.G.) (SHOWA, 99.5%). Detail chemical reduction mechanism of the solvent was introduced in other reports [14,15]. Pt (IV) metal ion concentration was fixed at 10 mM in a beaker. Then the solution was pre-heated under 160 °C for thermodynamic stabilization and reactants dipping rate was 2 ml min^{-1} till exhausted. After dipping, the entire reaction system was kept under 160 °C for 3 h under N_2 flux 25 cm^3 min^{-1}. The whole reaction system was kept under 120 rpm magnetic stirring by temperature programmed hot plate and reaction temperature was kept within ±1 °C. After acetone dilution, dark brown gelation precipitate formed as polymer and nanoparticle composites. Residual sample re-dispersed into EtOH and further centrifuged at 15 000 rpm for 5 h. After that, the MWCNTs/CC was directly impregnated into Pt–PVP/EtOH solution and dried in a furnace under 200 °C for removing contaminants.

2.3. Characterization of the MWCNTs electrode

The information of functional groups attached on modified MWCNTs was provided by a Fourier transform infrared spectroscopy (FT-IR, protege 460). A high resolution transmission electron microscopy (HRTEM, Philips Tecnai-20) was used to investigate the nanostructure of MWCNTs. Raman spectroscopy (Jobin Yvon Lab-RAM HR) was used for examining the structure of modified MWCNTs, using He–Ne laser with a wavelength of 632.8 nm. Electrocatalytic behaviors of Pt/MWCNTs electrode was investigated by cyclic voltammetry (CV) (CH Instrument 614B potentiostat) using a three-electrode cell. A platinum wire served as the counter electrode and a saturated calomel electrode (SCE), was used as the reference electrode. The working electrode is a Pt wire attached with a 0.25 cm^2 thin Pt foil, which is used to contact with the testing sample (Pt/MWCNTs).

3. Results and discussion

3.1. The characterizations of Pt/MWCNTs electrode

The FTIR spectra of untreated, conventional nitric acid treated and microwave digestion-treated MWCNTs are presented in Fig. 1. The peaks at about 1730 and 1590 cm^{-1} on FTIR spectra in Fig. 1(b) and (c) suggested that carboxylic acid groups and carboxylate groups and were presented on the surface for both conventional nitric acid-treated and microwave digestion-treated MWCNTs. The IR spectra of conventional nitric acid-treated and microwave digestion-treated MWCNTs show almost the same characteristic, which indicates the surface of microwave digestion-treated MWCNTs were functionalized in a short time. XPS of microwave digestion treated MWCNTs is presented in Fig. 2. The C 1 s spectrum appears to be composed of graphitic carbon (284.8 eV) and C═O like species (285.82 eV). A small amount of surface functional groups of –CO (286.8 eV) and –COO (290.14 eV) were also noted in the spectrum, which are the evidences of the functionalization of MWCNTs surface after acid-treatment by microwave digestion method. Raman spectra of pristine, nitric acid-treated, and micro-

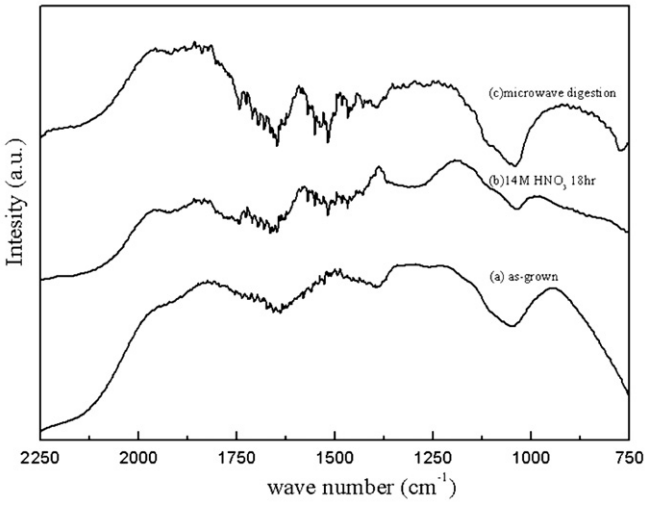

Fig. 1. FT-IR spectra of CNTs with and without modifications.

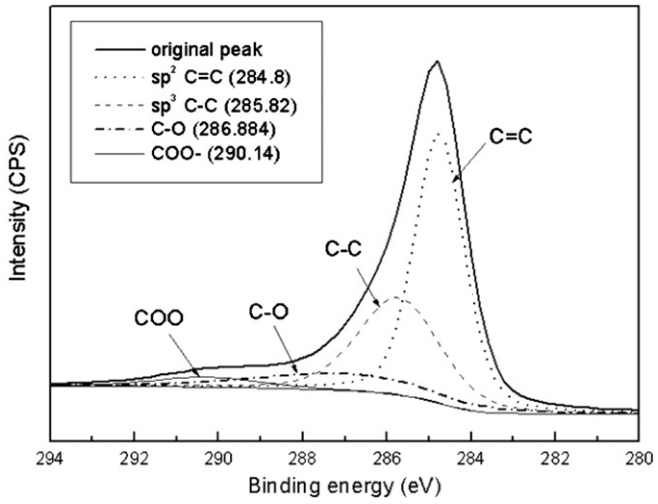

Fig. 2. XPS of microwave digestion treated MWCNT.

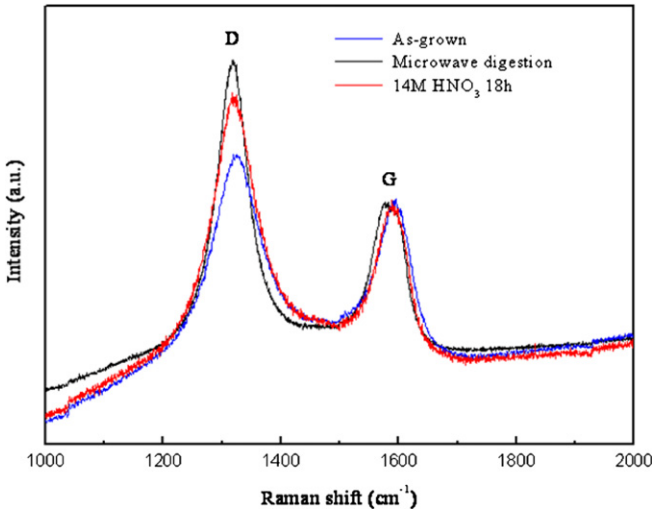

Fig. 3. Raman spectra of: (a) as-grown MWCNTs, (b) MWCNTs treated by 14 M HNO_3 solution for 18 h and (c) MWCNTs treated by microwave digestion method in 5 M HNO_3 solution.

wave digestion treated MWCNTs are shown in Fig. 3. All samples of MWCNTs show a disorder-induced peak around 1350 cm^{-1}, which roughly corresponding to the D-line associated with disorder-allowed zone-edge modes of graphite. After modifications, a significant increase of the intensity of D-band can be observed in Raman spectra. This is because the perfect two-dimensional graphitization is altered to a more disordered structure by carboxylation. The I_D to I_G ratio of these samples was calculated by integrating the area of D-band and G-band. The calculated I_D/I_G ratios of pristine, nitric acid-treated, and microwave digestion-treated MWCNTs were 1.34, 1.96, and 2.21, respectively. The high I_D/I_G ratio of MWCNTs indicates more functional groups on the surface of MWCNTs after modifications [16,17]. Fig. 4 depicts the HRTEM images of the nitric acid-treated and the microwave digestion-treated MWCNT. It can clearly be seen that the catalyst

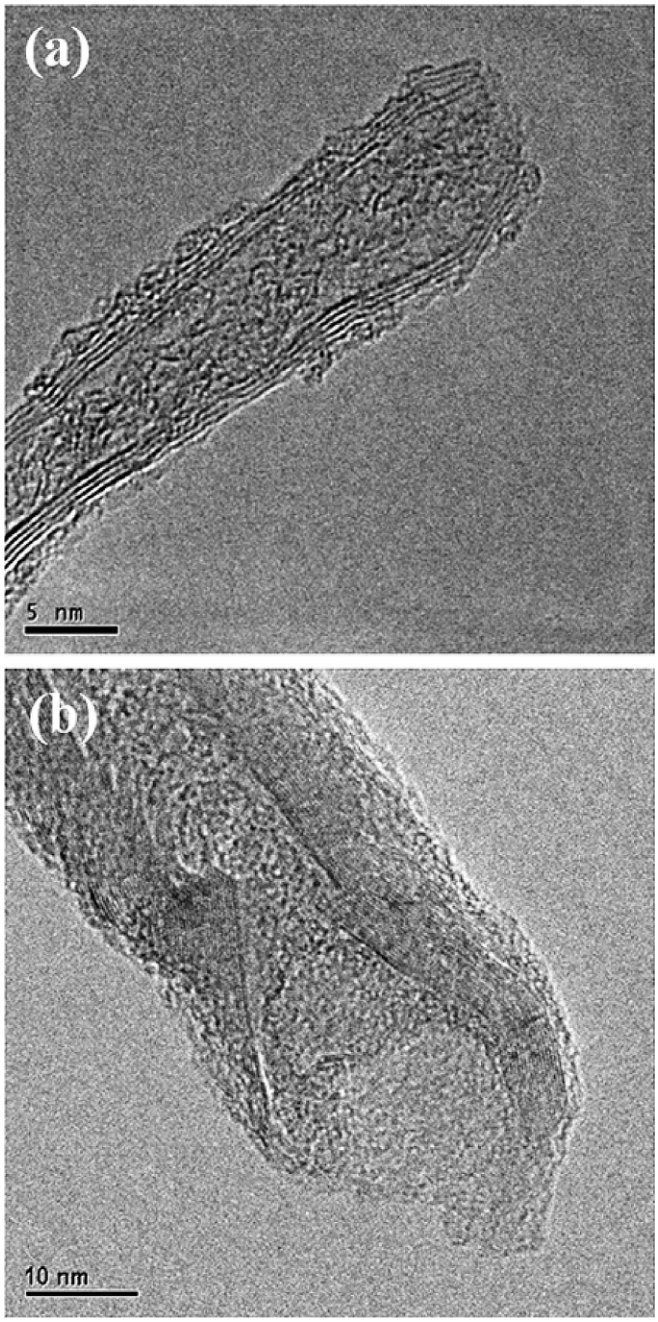

Fig. 4. HRTEM images of open-end MWCNTs which were synthesized: (a) by refluxing in 14 M HNO_3 for 18 h and (b) by microwave digestion method in 5 M HNO_3 solution.

embedded in the tip of the MWCNT was removed in both Fig. 4(a) and (b). It is believed that the nitric acid destroyed the cap of MWCNT first and then eliminated the catalyst. However, the surface of nitric acid treated MWCNT was damaged after acidic treatment for 18 h. On the contrary, microwave digestion takes a tremendous advantage because the acid in this approach can absorb microwave energy rapidly and dissolve metal efficiently without damaging the wall structure and the processing time could be reduced. The catalysts were loaded by impregnated 1 cm^2 MWCNTs electrode into 2 ml precursor with 2 mg metal

loading. However, the actual Pt loading for pristine, nitric acid-treated and microwave digestion-treated Pt/MWCNTs samples are 0.18, 0.24 and 0.30 mg/cm^2, which were determined by burning away the MWCNTs at 900 °C in O_2 atmosphere. We supposed that the nitric acid-treated MWCNTs by both methods can supported more Pt catalysts because of the functionalized surface and open-end structure of MWCNTs. It is identical with Raman results. TEM micrographs of Pt nanoparticles disperse on (a) pristine MWCNTs and (b) microwave digestion treated MWCNTs are shown in Fig. 5. The distribution of Pt nanoparticles on pristine MWCNTs is not uniform and large Pt clusters can be found. The significant agglomeration of Pt nanoparticles on MWCNTs is due to the chemically inert and hydrophobic surface of MWCNTs. However, a better dispersion of Pt nanoparticles on microwave digestion-treated MWCNTs is shown in Fig. 5(b). Although agglomeration of Pt nanoparticles still exists, the distribution of Pt nanoparticles on acid-treated MWCNTs by microwave digestion is greatly improved.

3.2. Electrochemical properties of Pt/MWCNTs electrode

The electrocatalytic activity of Pt catalyst was tested by cyclic voltammetry (CV) in electrolyte of 1.0 M H_2SO_4 with a scan rate of 50 mV s^{-1} and is shown in Fig. 6. In the range of the voltage between −0.1 and 0.2 V, several sharp peaks can be shown. Weak H-adsorption and strong H-adsorption peaks are observed during cathodic potential sweep between 0.4 and 0.05 V. The strong, medium and weak H-desorption peaks between 0.4 and 0.05 V are also observed under anodic sweep [18]. By using the charge passed for H-adsorption Q_H, surface area of Pt (S_{Pt}) can be estimated from the equation below [19]

$$S_{Pt}/cm^2 = Q_H/210\ (\mu C/cm^2) \quad (1)$$

The constant 210 in Eq. (1) is surface charge density of Pt. Each electrode was taken with a triangular potential sweep (50 mV s^{-1}) between 0.05 and 1.05 V (vs. SCE) in 1 M H_2SO_4 solution for the determination of the surface

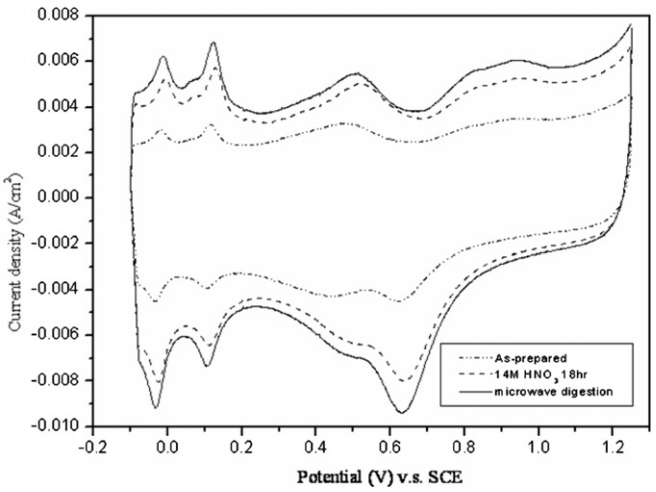

Fig. 6. Cyclic votammograms of Pt/CNTs electrode in 1.0 M H_2SO_4 aqueous solution with a scan rate of 50 mV s^{-1}.

area of Pt. Therefore, the calculated active surface area of Pt from Fig. 4 are 5.6, 20.1, and 23.9 cm^2 for the pristine, nitric acid-treated, and microwave digestion-treated MWCNTs. The microwave digestion-treated Pt/MWCNTs electrode has larger electrochemical Pt surface area than the others, which could be attribute to the more Pt amount attached on the MWCNTs and uniform distribution of Pt nanoparticles. Various electrochemical properties of these samples are listed in Table 1. Table 1 lists various calculated values of Pt loading (L_{Pt}, mg), working surface area of Pt (S_{Pt}, cm^2), methanol oxidation current density at 0.8 V (i, mA cm^{-2}) of samples and mass efficiency of Pt (Me, mA mg^{-1} Pt).

Electrocatalytic activities of Pt/MWCNTs electrodes in methanol solution which were measured in a deaerated 1.0 M CH_3OH + 1.0 M H_2SO_4 solution between 0 and 1.0 V with a scan rate of 50 mV s^{-1} are shown in Fig. 7. Methanol-oxidation current peaks are clearly observed at 0.8 V in the anodic sweep and at 0.6 V in the cathodic sweep from all samples, which represent the reactions of Eqs. (2) and (3) [20].

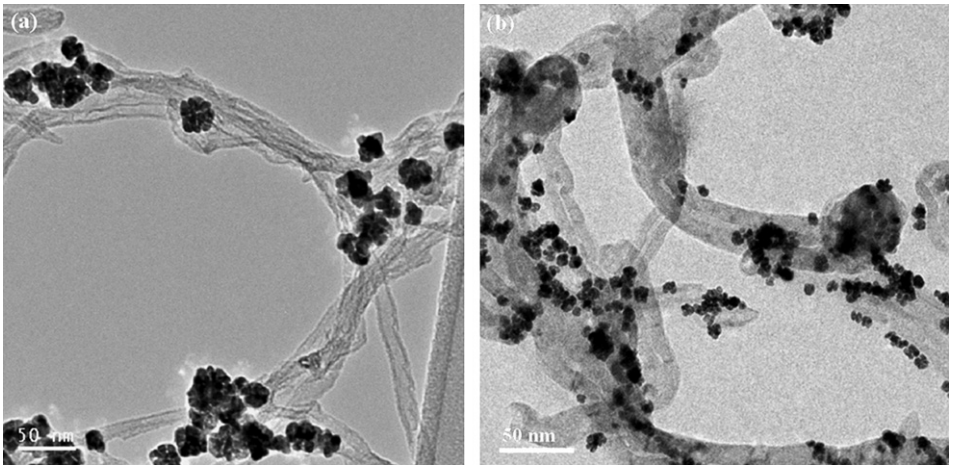

Fig. 5. TEM images of Pt nanoparticles disperse on: (a) pristine MWCNTs and (b) microwave digestion treated MWCNTs.

Table 1
Electrochemical properties of Pt/MWCNTs with various treatments

Sample	L_{Pt} (mg cm^{-2})	S_{Pt} (cm^2)	i(mA cm^{-2})	Me (mA mg^{-1}Pt)
Pristine MWCNTs	0.18	5.6	28	156
14 M HNO_3, 18 h	0.24	20.1	59	246
Mircowave digestion	0.30	23.9	76	253

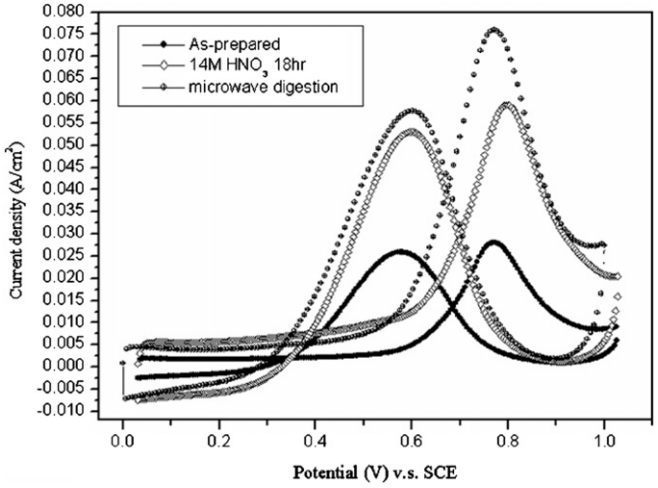

Fig. 7. Cyclic voltammograms of Pt/CNTs electrode in 1.0 M H_2SO_4 + 1.0 M CH_3OH aqueous solution with a scan rate of 50 mV s^{-1}.

$$Pt–(CH_3OH)ads \rightarrow Pt–(CO)ads + 4H^+ + 4e^- \quad (2)$$

$$Pt–CO + Pt–OH \rightarrow 2Pt + CO_2 + H^+ + e^- \quad (3)$$

The current density of methanol oxidation of microwave digestion-modified Pt/MWCNTs at 0.8 V is 76 mA cm^{-2}, which is higher than conventional nitric acid-treated sample and almost 2.5 times as high as the untreated Pt/MWCNTs sample. The Pt nanoparticles on modified MWCNTs show the higher utility than pristine MWCNTs from the comparison of mass efficiency in Table 1. This may be attributed to the functionalized surface and the presence of open-end MWCNTs, which Pt nanoparticles can uniformly disperse on MWCNTs with larger amount.

4. Conclusion

A fast and effective way for modifying MWCNTs was demonstrated in this paper. TEM images reveal that the modification by microwave digestion method can obtain undamaged and open-end MWCNTs. The aggregation of Pt nanoparticles can be greatly improved by functionalizing the surface of MWCNTs using the microwave digestion method. The CVs results show that the microwave digestion-modified Pt/MWCNTs electrode exhibits the larger electrochemical Pt surface area and higher current density of methanol oxidation than untreated and conventional nitric acid-treated Pt/MWCNTs electrodes. This technique can be widely used for effective modifying CNTs and shorting the process time.

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