A simple approach towards sulfonated multi-walled carbon nanotubes supported by Pd catalysts for methanol electro-oxidation

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ABSTRACT

Functionalized benzenesulfonic groups were grafted onto the surface of multi-walled carbon nanotubes (MWCNTs) supported Pd catalysts in direct methanol fuel cells by a new and simple *in situ* radical polymerization of 4-styrenesulfonate and isoamyl nitrite. The resultant sulfonated MWCNTs-supported Pd catalysts (S-MWCNTs/Pd) were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and Fourier transform infrared (FTIR) spectrometry measurements. Electrochemical characterizations of S-MWCNTs/Pd catalysts for methanol electro-oxidation in alkaline solution were investigated by cyclic voltammetry techniques. These results showed that S-MWCNTs/Pd exhibited higher electrocatalytic activity, enhanced CO tolerance and better stable life than did that with the unsulfonated counterparts, mainly due to the easier access with methanol and well dispersed distribution of the S-MWCNTs/Pd catalysts in water. In addition, compared with traditional sulfonation of MWCNTs, this new approach is more advantageous to make small and uniform dispersion of Pd particles loaded onto the surfaces of sulfonated MWCNTs, indicating it is a simple, rapid, and efficient method to functionalize MWCNTs.

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1. Introduction

There is an increasing interest in electro-oxidation of methanol in view of the development of direct methanol fuel cells (DMFCs) as power sources for electric vehicles and electronic devices [1]. DMFCs is a promising technology as an alternative to conventional energy-generating devices due to its higher energy-conversion efficiency, low-to-zero pollutant emissions, ready availability of methanol fuel, ease in distribution, and high energy density [2,3]. The commercialization of DMFCs, however, is still significantly restricted by its high cost, mainly caused by the low utilization of novel metal in the catalytic electrode. The electrocatalytic activity towards noble metals for methanol oxidation is greatly dependent on many factors such as the size and dispersion of noble metals, properties of supporting materials and synthetic methods [4,5]. Among them, the properties of supporting materials and their surface characteristics are essential for the catalysts materials to produce high catalytic activity [6,7].

Nanostructured carbon materials, especially one-dimensional (1D) carbon nanotubes (CNTs), appear to be one of the most promising supporting materials, such as for new chemical nanoarchitectures in electrocatalysis [8,9] and nanoelectronic circuitry [10], due to their unique structure and excellent mechanical, electronic and surface properties [11]. Much work has focused on the dispersion of metal nanoparticles on the surface of CNTs as catalysts for fuel cells. Much work has focused on synthesis of highly dispersed metal nanoparticles on the surface of CNTs as catalysts for fuel cells [8,10,12–14]. However, the pristine surface characteristics of CNTs are relatively inert and difficult to homogeneously support metal particles, which directly affect the catalytic efficiency of electrode. Chemical modification is a common method and is essential for the deposition of catalysts and other species onto the surface of carbon nanotubes for nanocatalytic applications [15,16]. The conventional chemical modification procedures involve oxidation with acids or ozone, during which the oxygenated functionalities such as carboxylic acid esters or quinines were generated on the carbon surface. Nevertheless, the drawback with this modification technique lies in the low surface reactivity and the damage to the carbon materials during the oxidative treatment [17].

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Recently, sulfonation methods formed covalent or non-covalent bond on carbon nanotube by oxidation of diazonim salts, thermal decomposition of sulfuric acid, microwave-enhanced chemical modification and electrochemical reduction, which has been proved to be the novel and efficient modification method [18–21]. Considering the recent interest in the use of multi-walled carbon nanotubes (MWCNTs) from both modification point of view and metal nanoparticle catalyst supports, we can find some examples of metal nanoparticle deposition on sulfonated MWCNTs in the literatures. Wang et al. reported Pt nanoparticles deposited onto the sulfuric acid groups modified MWCNTs by thermal decomposition method [19]. Waje et al. synthesized Pt catalysts by adsorbing $[PtCl_6]^{2-}$ onto the sulfonic acid groups modified CNTs through electrochemical reduction [21]. Du et al. took advantage of traditional polymerization of 4-styrenesulfonate to decorate Pt/MWCNTs catalyst with benzenesulfonic groups [22]. It is noteworthy that sulfonation of carbon nanotube-supported Pt catalysts is a useful modification approach to improve the electrochemical performance of Pt catalysts, but most of the methods are generally complicated, especially complex process controls are involved. Therefore, the preparation of sulfonation functionalized carbon nanotube-supported metal catalysts by a simple and controllable method is still required.

In the present work, we demonstrate a new approach to sulfonation of MWCNTs directly by in situ radical polymerization of 4-styrenesulfonate and isoamyl nitrite at ambition temperature, which is schematically illustrated in Fig. 1. The Pd catalysts supported on sulfonated MWNTs were characterized by transmission electron microscopy (TEM), Fourier transform infrared (FTIR), X-ray diffraction (XRD), cyclic voltammetry and chronoamperogram techniques in detail. Compared to previous methods for the treatment of carbon nanotubes [18,19,22], this method is more simple, rapid, and effective. The MWCNTs/Pd synthesized in this way exhibited a high catalytic activity, good CO tolerance and stable life for methanol electro-oxidation, which indicates that it has potential application in fuel cells.

2. Experimental

2.1. Catalysts synthesis

MWCNTs (20–40 nm in diameter) used in this work were produced via chemical vapor deposition method and purified according to Ref. [23,24], named as P-MWCNTs.

The simple sulfonation approach for MWCNTs was based on the in situ radical polymerization of acetic anhydride and concentrated sulfuric acid [25]. Specifically, some isoamyl nitrite was stirred with a proper amount of P-MWCNTs and 4-styrenesulfonate for 1 h at room temperature. Then the reaction temperature was gradually raised to 70 °C, and kept for 2 h. The resulting product was repeatedly washed with dimethylformamide and hot chloroform three times, and then dried at 70 °C overnight in a vacuum oven. The obtained sample was denoted as S-MWCNTs.

For comparison, we also prepared another typical sulfonation approach for MWCNTs using the in situ radical polymerization of 4-styrenesulfonate, according to [26], named as F-MWCNTs. First, a mixture of 96% H_2SO_4 was stirred with a proper amount of P-MWCNTs and $(NH_4)_2S_2O_8$ for 6 h, then the substituted 4-aminobenzenesulfonic acid was added and homogenization was continued for 2 h. Second, predetermined amount of $NaNO_2$ and 2,2-azobisisobutyronitrile was added, the mixture was well agitated at 80 °C for 6 h. The resulting product was filtered and washed with deionized water, acetone, and fresh N,N-dimethylformamide then dried at 70 °C overnight in a vacuum oven.

S-MWCNTs-supported Pd catalysts were synthesized by using $NaBH_4$ as a reductive agent at a room temperature [27]. Two milliliters of 6 mg/mL $PdCl_2$ solution were dissolved in deionized water, and then 60 mg S-MWCNTs were added to this solution. The $NaBH_4$ solution ($NaBH_4$/metal molar ratio = 8) was slowly dropped into this mixture and vigorously stirred for 12 h. The resulting slurry was filtered, washed thoroughly with deionized water and then dried in a vacuum oven. The metal loading on S-MWCNTs was determined to be 16.1 wt.%. For comparison, the P-MWCNTs/Pd and F-MWCNTs/Pd catalysts were synthesized under the same procedure.

2.2. Preparation of electrodes

Glassy carbon (GC) working electrodes, 3 mm in diameter (electrode area 0.12 cm^2), were used as the substrates for MWCNTs-supported catalysts. Five milligrams catalysts were added into 1 mL 0.05 wt.% Nafion solution, and the mixture was treated 20 min with ultrasonication for uniform dispersion. A measured volume (25 μL) of this mixture was dropped by a micropipette onto the top surface of the GC electrode. The modified GC electrode was employed as the working electrode in our experiments.

2.3. Instrument and measurement

XRD analysis was carried out on Bruker D8-ADVANCE diffractometer with Cu Kα radiation of wavelength λ = 0.15418 nm. Transmission electron microscopy (TEM, FEI Tecnai G2 20 S-TWIN) operating at 200 kV was applied to characterize the morphology and particle size distribution. Infrared spectra were recorded with a model 360 Nicolet AVATAR FT-IR spectrophotometer.

The cyclic voltammetry measurements were performed with CHI 660C electrochemical work station (Shanghai, China), a conventional three-electrode system was used throughout this work. The working electrode is a modified glassy carbon electrode (GCE), Pt foil was used as counter electrode and saturated calomel electrode (SCE) was reference electrode, respectively. All the electrolytes were deaerated by bubbling nitrogen (N_2) for 20 min and protected with a N_2 atmosphere during the experimental procedure. All the experiments were carried out at a temperature of 25 ± 1 °C.

3. Results and discussion

3.1. FTIR analysis

The possibility of F-MWCNTs with benzenesulfonic group, which was sulfonated by in situ radical polymerization of 4-styrenesulfonate, has been examined by the FTIR spectrum in our previous work [13]. Here we use FTIR analysis of S-MWCNTs to confirm such interaction, for the in situ radical polymerization of 4-styrenesulfonate with soamyl nitrite, is shown in Fig. 2. The sample synthesized with 4-aminobenzenesulfonic acid shows characteristic peaks at 1601, 1578, 1499, 1423 cm^{-1} (aromatic C=C), 1009 and 1123 cm^{-1} (=CH), 1634, 2878 and 2882 cm^{-1} (−CH), and 834 cm^{-1} (C−H para-aromatic out of plane vibration), 686, 1041 and 1169 cm^{-1} (−SO$_3$) [28,29]. These representative absorption peaks indicated that benzenesulfonic groups were successfully modified on the surface of S-MWCNTs. It also proven that the functionalized process of S-MWCNTs was in good accordance with Fig. 1.

3.2. Dispersibility analysis

The dispersibility of P-MWCNTs, F-MWCNTs and S-MWCNTs in water were evaluated 240 h after the ultrasonic dispersion (Fig. 3). A lot of P-MWCNTs depositions are found at the bottom of vials
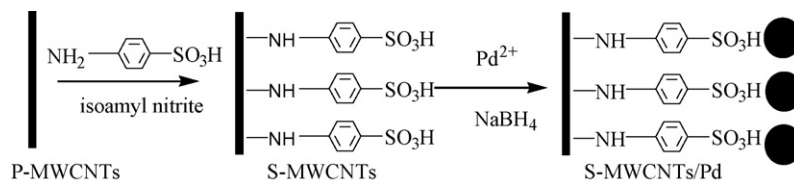
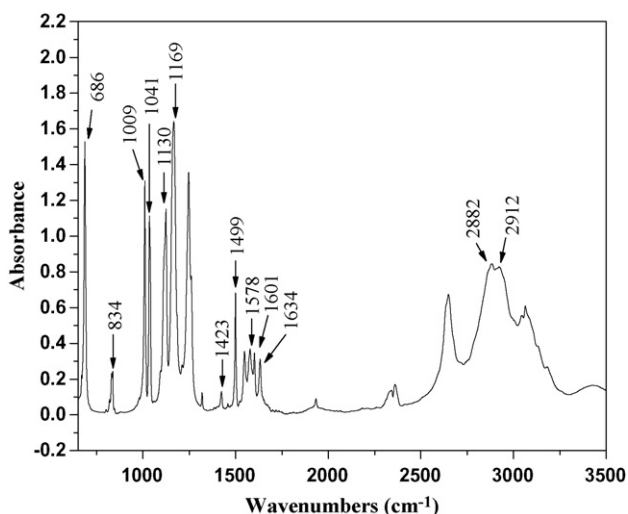Fig. 1. Schematic illustration of the synthesis of S-MWCNTs/Pd.

Fig. 2. FTIR spectra of S-MWCNTs.

in water (Fig. 3a). In contrast, it is noted that both F-MWCNTs and S-MWCNTs exhibit homogeneous dispersion in water even after 240 h (Fig. 3b and c). The result clearly indicated that the benzenesulfonic groups functionalized MWCNTs were successfully formed,

where hydrophilic benzenesulfonic groups greatly improved the dispersibility of modified MWCNTs.

3.3. XRD analysis

It can be seen from Fig. 4, the sharp diffraction peaks around 25.8° are attributed to the graphite structure (0 0 2) reflection of MWCNTs. The other featured peaks could be indexed to the (1 1 1), (2 0 0) and (2 2 0) reflections of Pd crystal, which was well consistent with previous results [13,28]. As for S-MWCNTs/Pd and F-MWCNTs/Pd catalysts, they show significantly broader peaks than those of P-MWCNTs/Pd catalysts, indicating that small sizes of Pd nanoparticles were loaded on these carbon supports. The mean sizes of Pd nanoparticles on the P-MWCNTs/Pd, F-MWCNTs/Pd and S-MWCNTs/Pd catalysts were calculated to be 5.2, 4.3 and 4.1 nm, respectively, from the broadening of the (2 2 0) diffraction peaks using Scherrer's equation.

3.4. TEM analysis

The significant decrease in Pd nanoparticles size was probably due to the chemically active and hydrophilic surface of MWC-NTs after benzenesulfonic functionalization. Fig. 5a shows the TEM image of P-MWCNTs. It has a relatively random dispersion of the
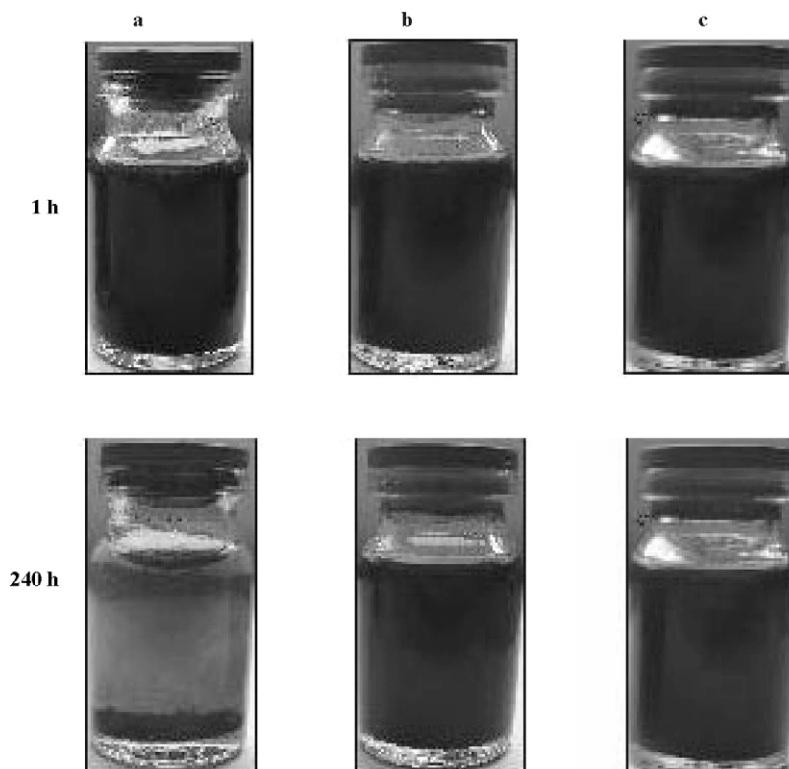

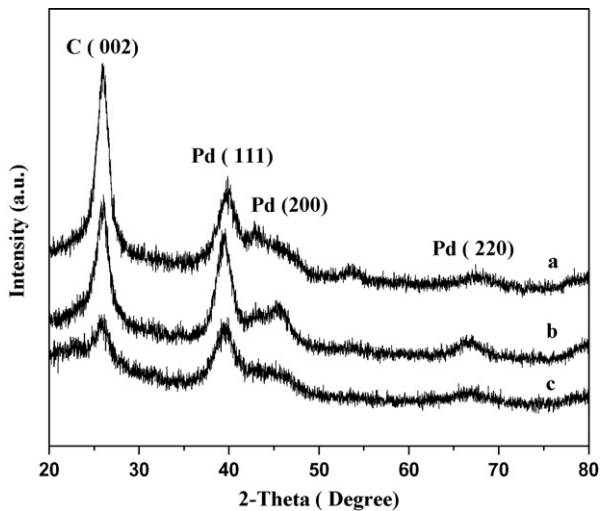Fig. 3. Dispersibility of three MWCNTs in water solution: (a) P-MWCNTs; (b) F-MWCNTs; (c) S-MWCNTs.

Fig. 4. XRD patterns of three catalysts: (a) F-MWCNTs/Pd; (b) P-MWCNTs/Pd; (c) S-MWCNTs/Pd.

metal particles, and large Pd aggregation somewhere. However, both the F-MWCNTs and S-MWCNTs samples exhibit the metal particles are dispersed on the carbon support uniformly, and almost have a similar particle size of approximately 4 nm, in good agreement with the XRD results. It should be mentioned that the carbon nanotubes were decorated with the hydrophilic amine group after benzenesulfonic functionalization, and the solution became a uniform and inky suspension in water. Therefore, in the case of adding $NaBH_4$ as reducing agent, well dispersed and highly orientated Pd particles supported on the carbon nanotubes can be easily prepared by the chemical process.

3.5. Electrochemical measurements

The electrochemical catalytic activities toward the oxidation of methanol of three carbon-supported Pd (16.1 wt.%) catalysts were investigated through cyclic voltammetrys. As can be seen from Fig. 6, the three catalysts show the similar feature, where one can observe a typical methanol oxidation peak in the forward scan and another oxidation peak in the backward scan corresponding to the removal of the residual carbon species formed in the forward scan [27,30]. For the S-MWCNTs/Pd catalysts, the current density ini-
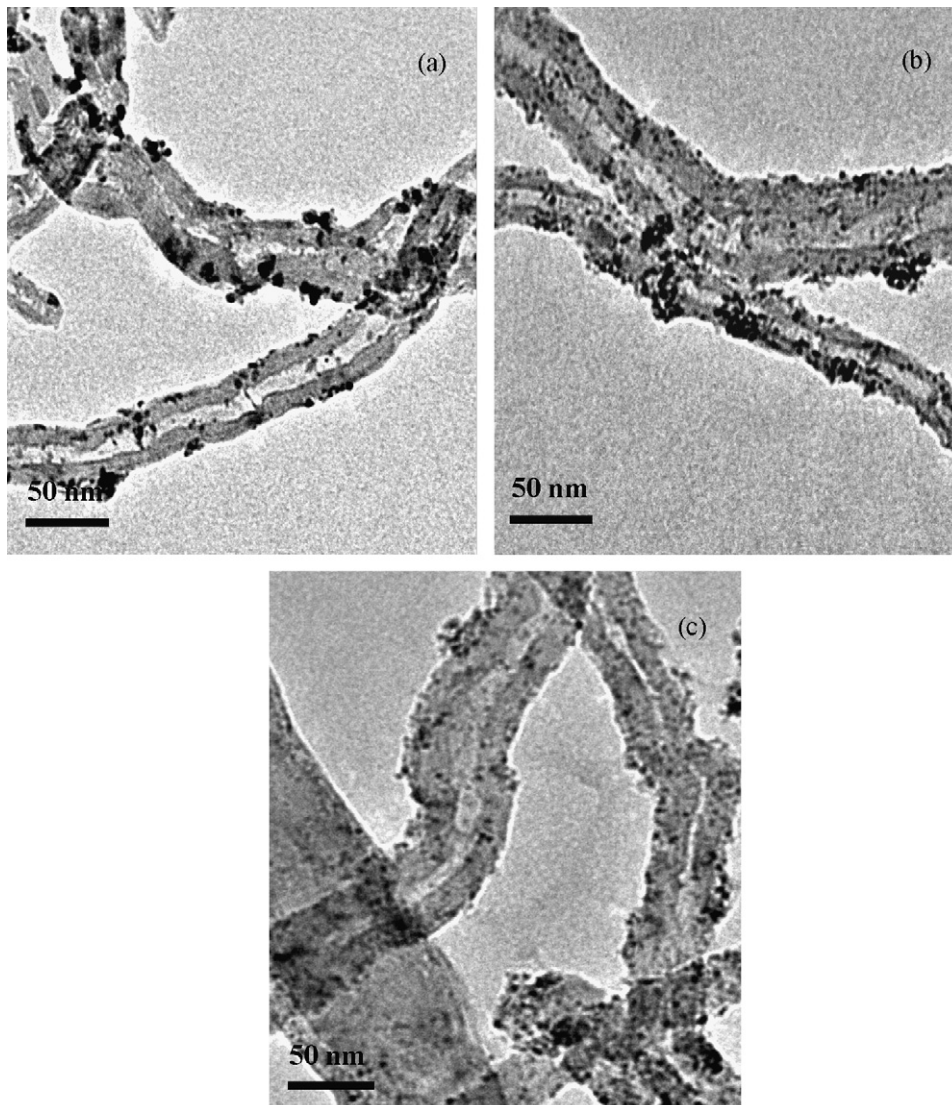

Fig. 5. TEM patterns of three catalysts: (a) P-MWCNTs/Pd; (b) F-MWCNTs/Pd; (c) S-MWCNTs/Pd.
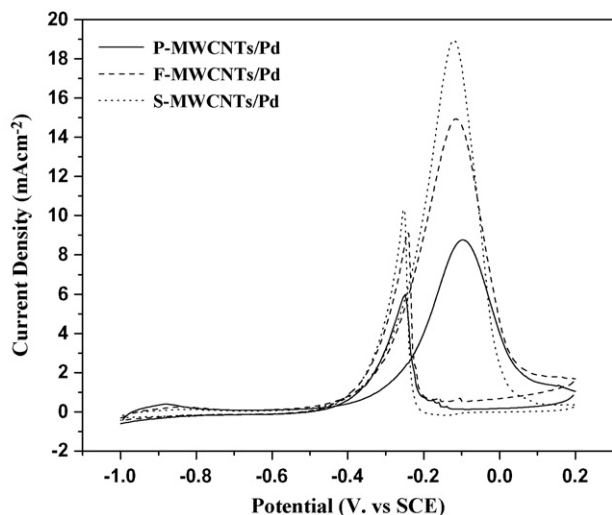
Fig. 6. Cyclic voltammograms of three catalysts in N_2 saturated aqueous solution of 1.0 M CH_3OH in 0.5 M KOH at a scan rate of 5 mV s^{-1}.

Fig. 7. Current–time curves of three catalysts in N_2 saturated aqueous solution of 1.0 M CH_3OH in 0.5 M KOH at a fixed potential of −0.2 V.

tially rose above the background level at about −0.43 V (the "onset potential"), which was more negative than that of P-MWCNTs/Pd catalysts (at about −0.41 V) and F-MWCNTs/Pd catalysts (at about −0.37 V). The more negative onset potential suggested that S-MWCNTs/Pd catalysts had a positive effect on promoting the oxidation of methanol by lowering its overpotential. Additionally, the current density increased to 19.01 mA cm^{-2} at the potential range of −0.10 to 0.05 V, which was two times of the corresponding current density (8.76 mA cm^{-2}) obtained on F-MWCNTs/Pd catalysts in the same range. Furthermore, F-MWCNTs/Pd catalysts presented a maximum current density of 14.91 mA cm^{-2}, which was also much lower than that of S-MWCNTs/Pd catalysts.

Yet another method to benchmark the catalyst performance is compare the ratio of current density associated with the anodic peaks in the forward (I_f) and reverse (I_b) scans. Such a ratio has been used to infer the CO tolerance of the catalysts [7,19]. A lower I_f/I_b value indicates poor oxidation of methanol to CO during the anodic scan and excessive accumulation of residual carbon species on the catalyst surface, in other words, a greater extent of CO poisoning. Hence a higher I_f/I_b value is indicative of improved CO tolerance. The I_f/I_b values of the three differently catalysts are listed in Table 1. It can be seen that S-MWCNTs/Pd catalysts has the highest I_f/I_b, indicating the best CO resistance.

Chronoamperometric technique is an effective method to evaluate the electrocatalytic activity and stability of catalyst materials. Fig. 7 shows the typical current density–time responses of three Pd-based catalysts for methanol electro-oxidation. 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 Pd oxides and/or adsorbed intermediates in methanol electro-oxidation reaction [27,30,31]. As expected, the methanol oxidation current of S-MWCNTs/Pd catalysts was evidently higher than that of other two catalysts. In the steady-state region, S-MWCNTs/Pd catalysts presented the current density of (33.72 mA cm^{-2}) after 500 s, while F-MWCNTs/Pd and P-MWCNTs/Pd catalysts exhibited current
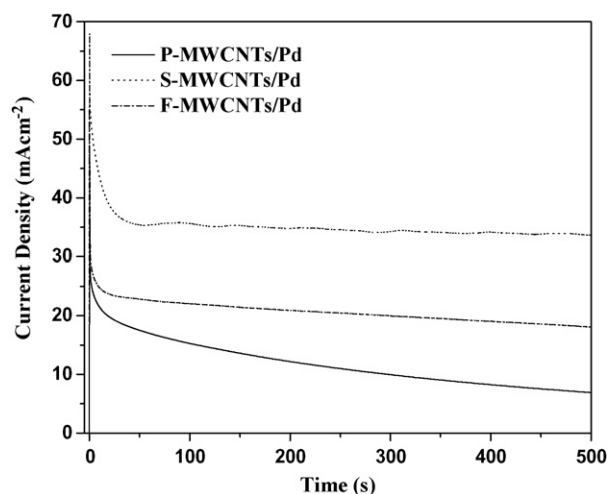
density of about 18.06 and 6.88 mA cm^{-2}, respectively. All results indicated that the S-MWCNTs/Pd catalysts had the best electrocatalytic stability among three catalysts. In other words, S-MWCNTs catalysts showed superior electrocatalytic performance including higher catalytic activity and better stable life for methanol oxidation than did that with counterpart sulfonated by the traditional functionalized method. What is more, the current density of S-MWCNTs/Pd catalysts behaved with a more gently decreasing trend, which was also possibly owing to architectures of S-MWCNTs support.

According to the above results, S-MWCNTs/Pd shows the best electrochemical performance including activity, CO tolerance and stability toward ethanol oxidation among three Pd-based catalysts. The reasons may be as follows: (1) the deposition of Pd originated from Pd salt ions can thus take place on the S-MWCNTs surface. However, it will be severely hindered by the presence of the compact layer of benzenesulfonic groups. The deposition of Pd on S-MWCNTs most likely takes place at the sulfonic acid functional groups on the organic molecules attached. This avoids the problems of aggregation and non-uniform size distribution associated with direct deposition of Pd on S-MWCNTs surface; (2) although there is small probability of some Pd deposition directly on the S-MWCNTs surface, in this case again the existed presence of bulky organic groups will act as barriers and hence avoid the aggregation of Pd nanoparticles in the subsequent reduction step; (3) the special frame and properties of Pd-hydrophilic groups–MWCNTs hybrids may be helpful to facilitate the transmission of the electrolyte and methanol through the surface of the catalyst [23,32,33]. In other words, the liquid reactants might facilely diffuse onto the surface of the catalyst and thus reduce the liquid sealing effect greatly, which would enhance the active surface area for electrochemical reactions. It is worth noting that the experiments discussed here not been optimized. At present, the further investigations will be required to address this question.

4. Conclusion

In summary, ordered sulfonated MWCNTs derived from *in situ* radical polymerization of 4-styrenesulfonate and isoamyl nitrite was employed by a simple, rapid, practical strategy. The method is effective for the functionalization and dispersibility of carbon nanotubes. Furthermore, the uniform and highly dispersed Pd nanoparticles supported on the novel carbon support were synthe-

Table 1
Comparison of electrocatalytic properties of three different catalysts

Catalyst	Onset potential (V)	Current density (mA cm^{-2})	I_f/I_b
P-MWCNTs/Pd	−0.37	8.75	1.49
F-MWCNTs/Pd	−0.41	14.91	1.65
S-MWCNTs/Pd	−0.43	19.01	1.78

sized by a facile $NaBH_4$ assisted chemical reduction. It was found that well-dispersed, small particles were anchored onto the external walls of S-MWCNTs, and the size range of these particles was about 3–6 nm. Additionally, S-MWCNTs/Pd catalysts showed superior electrocatalytic performance including higher catalytic activity, enhanced CO tolerance and better stable life for methanol oxidation than did those with the unsulfonated counterpart. This simple, rapid and practical functionalized carbon nanotubes approach will lead to the development of a broad new class of materials with enhanced properties and even introduce new functionalities to carbon-based composites.

Acknowledgments

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