Short communication

A facile approach towards sulfonate functionalization of multi-walled carbon nanotubes as Pd catalyst support for ethylene glycol electro-oxidation

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ABSTRACT

Functional sulfonic acid groups were covalently grafted onto the surface of multi-walled carbon nanotubes (MWNTS) via a facile route from sulfuric acid and acetic anhydride under mild conditions. The resulting sulfonated MWNTS (S-MWNTS) were further deposited with Pd nanoparticles (S-MWNTS/Pd) as catalysts for ethylene glycol electro-oxidation. Structural characterizations revealed that homogeneously dispersed Pd nanoparticles with an average size of 4.5 nm were loaded on the S-MWNTS supports. It was found that S-MWNTS/Pd catalysts exhibited better electrocatalytic activity and long-term stability than the unsulfonated counterparts. In contrast to the common sulfonication approaches, our strategy could make the functionalization process more easily and effectively, in this way resulting in small size and uniform dispersion of Pd nanoparticles loaded onto the nanotube surfaces. All these demonstrate that it is a simple and efficient approach towards sulfonate-assisted surface functionalization.

1. Introduction

Since the discovery of the carbon nanotubes (CNTs) in 1991, there are tremendous interesting aspects on their characterization and potential application in various fields [1–9]. Considering the unique structural and excellent mechanical, electronic and surface properties [10], CNTs appear to be one of promising supporting materials in electrocatalysis [11–13]. Unfortunately, realistic applications have been greatly hindered by difficulties associated with processing. In principle, metal nanoparticles preferred absorbtion at the defect sites on the surface, not on sidewall of pristine carbon nanotubes [8,9,14]. It generally leads to poor dispersion and bad stability of metal nanoparticles on carbon supports. To resolve this issue, the surface of carbon nanotubes must be modified via a proper functionalization process [15–19].

Grafting functional sulfonic acid groups has been proven to be one of the ideal functionalization of CNTs by formation of covalent or non-covalent bond [3,4,20–22]. Typical synthetic routes include acid-assisted thermal decomposition, electrochemical modification, and chemical reduction method [17,20–26]. Acid-assisted thermal decomposition method involves refluxing CNTs with concentrated acids under high temperatures. Such aggressive treatments could destroy structural frameworks on the tip with the limited yields [20]. Electrochemical modification route allows mild operational conditions, whereas its utility is only restricted to electrically contacted CNTs on confined electrode surface [21,25]. In the case of aryl-functionalized CNTs by conventional chemical reduction method, the procedure is usually time-consuming, especially complex processes or multiple steps are involved in [22,26]. Consequently, there is an urgent need for the development of a facile and large-scale approach to produce sulfonate-functionalized CNTs as catalyst supports for fuel cells. Recently, Marietta et al. [24] proposed a simple synthetic route in which functional sulfonic acid groups were derived from concentrated sulfuric acid and acetic anhydride under mild conditions. But up to now there are no papers of using sulfonate-functionalized CNTs by this novel process as the supports of Pd nanoparticles in direct alcohol fuel cells. So this research work will be of great significance. In our previous work, we reported that sulfonated CNTs derived from in situ radical polymerization of sodium nitrite or isoamyl nitrite was employed through a simply approach, which was used as support for Pd catalysts [4].

Herein, a facile sulfonation approach has been proposed to graft functional sulfonic acid groups onto the MWNTS surfaces as promising supports for Pd catalysts. As demonstrated in Fig. 1, functional sulfonic acid groups were firstly introduced onto the surface of MWNTs under a rather mild circumstance. Then Pd^{2+} were uniformly anchored to the MWNTS surfaces via electrostatic interactions between the Pd^{2+} and the negatively charged sulfonic acid groups [5], which was expected to prevent agglomeration

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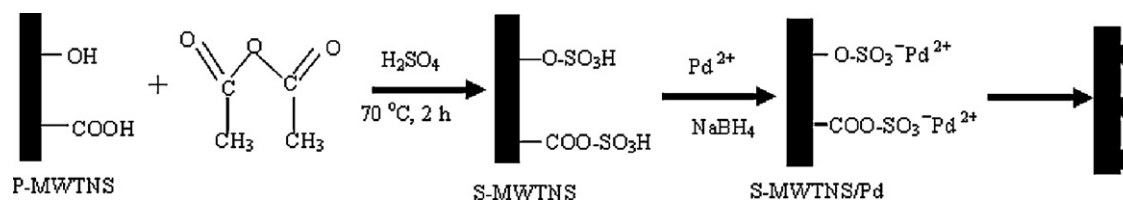E-mail addresses: liang@mpip-mainz.mpg.de (Y.-Y. Liang), lihl@lzu.edu.cn (H.-L. Li).

Fig. 1. Schematic illustration of the synthesis procedure of the composite.

of Pd nanoparticles on MWNTS surfaces. Additionally, grafting hydrophilic sulfonic acid groups could greatly improve the dispersibility of MWNTS in water. Furthermore, the current synthetic route is more controllable and operational conditions are gentler in contrast to our previous work concerning sulfonate functionalization of CNTs via in situ radical polymerizations. The as-prepared S-MWNTs/Pd catalysts exhibited better electrocatalytic activities and long-term stability for ethylene glycol (EG) electro-oxidation.

2. Experimental

2.1. Catalysts synthesis

MWNTS (20–40 nm in diameter) used in this work were produced by a chemical vapor deposition method, which were denoted as P-MWNTS. The process of preparation and purification are described in detail elsewhere [27]. In a typical experiment of synthesis of S-MWNTs, 100 mg of P-MWNTS was added to a mixture of 20 mL of sulfuric acid (H_2SO_4, 96%) and 300 mL of acetic anhydride ((CH_3-CO)$_2$O), holding continuous stirring at 70 °C for 2 h. After 2 h, the reaction mixture was cooled and unceasingly stirred until room temperature. The resulting product was repeatedly washed with distilled water and dried at 70 °C overnight in a vacuum oven. For comparison, we also prepared typical sulfonation approach from P-MWNTS using an in situ radical polymerization of 4-aminobenzenesulfonic acid [22], named as F-MWNTs.

S-MWNTS-supported Pd catalysts were synthesized by using $NaBH_4$ as a reductive agent. Two milliliters of 6 mg mL^{-1} $PdCl_2$ solution were dissolved in deionized water, and then 60 mg S-MWNTS were added to this solution. After that 40 mL $NaBH_4$ solution (0.02 M) was slowly dropped into this mixture and vigorously stirred at room temperature for 12 h. The resulting slurry was repeatedly washed with distilled water and dried in a vacuum oven. The P-MWNTS/Pd and F-MWNTS/Pd with the same Pd contents of around 20% were prepared 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 MWNTS-supported catalysts. Five milligrams catalysts were added into 1 mL 0.05 wt.% Nafion solution, and the mixture was treated 20 min with ultrasonication to form uniform dispersion. A measured volume (25 μL) of this mixture was dropped by a micropipette onto the top surface of the GC electrode.

2.3. Instrument and measurement

XRD analysis was carried out on Bruker D8-ADVANCE diffractometer with Cu Kα radiation (wavelength λ = 0.15418 nm). Transmission electron microscopy (TEM, FEI Tecnai G^2) operating at 200 kV was applied to characterize the morphology and particle size distribution. Energy dispersive spectroscopy (EDS) spectrum analysis was carried out on the same apparatus (FEI Tecnai G^2). Infrared spectra were recorded with a model 360 Nicolet AVATAR

FTIR spectrophotometer. Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Jarrell-Ash 1100) was used to analyze the Pd loadings on the catalysts.

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 GC electrode, 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 room temperature.

3. Results and discussion

Fig. 2 shows FTIR spectra of MWNTS before and after sulfonation functionalization, respectively. In comparison to P-MWNTS, the FTIR spectra of S-MWNTS exhibited the 682, 1726 and 1382 cm^{-1}, which could be attributed to the stretching modes of sulfonic acid groups [26,28]. All mentioned peaks could be attributed to the presence of sulfonic acid groups successfully grafted on the surface of MWNTS.

XRD patterns revealed bulk structure of the catalysts and supports. It could be observed from Fig. 3 that the typical peak located at a 2θ value of about 26° was referred to (0 0 2) reflection of MWNTS supports. The other featured four peaks were indexed to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) reflection of face centered cubic (fcc) crystalline Pd (JCPDS, Card No. 05-0681) [22,26]. As for F-MWNTS/Pd and S-MWNTS/Pd, they displayed significantly broader peak reflections than those of P-MWNTS/Pd catalysts, indicating smaller size of Pd catalysts were loaded on these carbon supports. Based on the (2 2 0) diffraction peaks using Scherrer's formula, the mean size of Pd crystallite on S-MWNTS/Pd, F-MWNTS/Pd and P-MWNTS/Pd were 4.5, 4.8 and 5.5 nm, respectively.
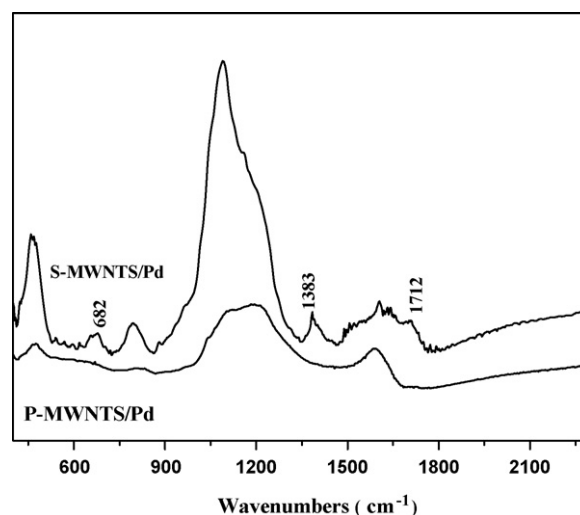

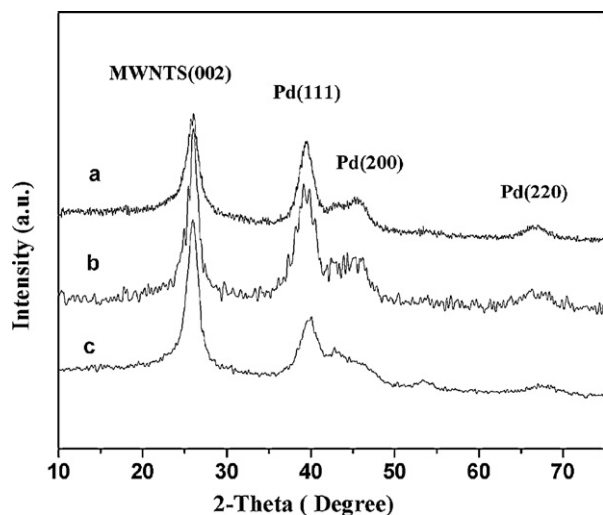**Fig. 2.** FTIR spectras of P-MWNTS and S-MWNTS.

Fig. 3. XRD patterns of three catalysts: (a) P-MWNTS/Pd, (b) F-MWNTS/Pd and (c) S-MWNTS/Pd.

Further investigation on the morphology of the Pd catalysts was conducted with TEM technology. As shown in Fig. 4a, P-MWNTS had a relatively random dispersion of Pd nanoparticles ranging from 4 to 7 nm, and apparent Pd aggregation could be observed somewhere. As for the F-MWNTs/Pd and S-MWNTs/Pd, most of the Pd nanoparticles were uniformly dispersed on the carbon supports with an average particle size of approximately 4–5 nm (Fig. 4b and c). Moreover, the EDX spectrum (Fig. 4d) revealed the existence of Pd, S and C species, reasonably derived from sulfonic acid groups successfully grafted on the outer walls of the MWNTS.

Fig. 5 was the statistical results counted from more than 200 Pd nanoparticles showing the distribution of the particle size. The size distributions of Pd nanoparticles on S-MWNTS (Fig. 5b) and F-MWNTS (Fig. 5c) were smaller than that supported on P-MWNTS (Fig. 5a). It should be mentioned that the carbon nanotubes were decorated with the hydrophilic sulfonic acid groups, providing uniform functional sites for absorption of Pd^{2+}, which could effectively prevent the preferred nucleation taking place at the defects on the surface of MWNTs [25]. Accordingly, well-dispersed and small-sized Pd particles could be easily accessible by the $NaBH_4$-assisted chemical reduction process.

Electrochemical performance of the resultant catalysts was firstly characterized through cyclic voltammetry. It was found that the electrochemically active surface area for S-MWNTS/Pd catalyst
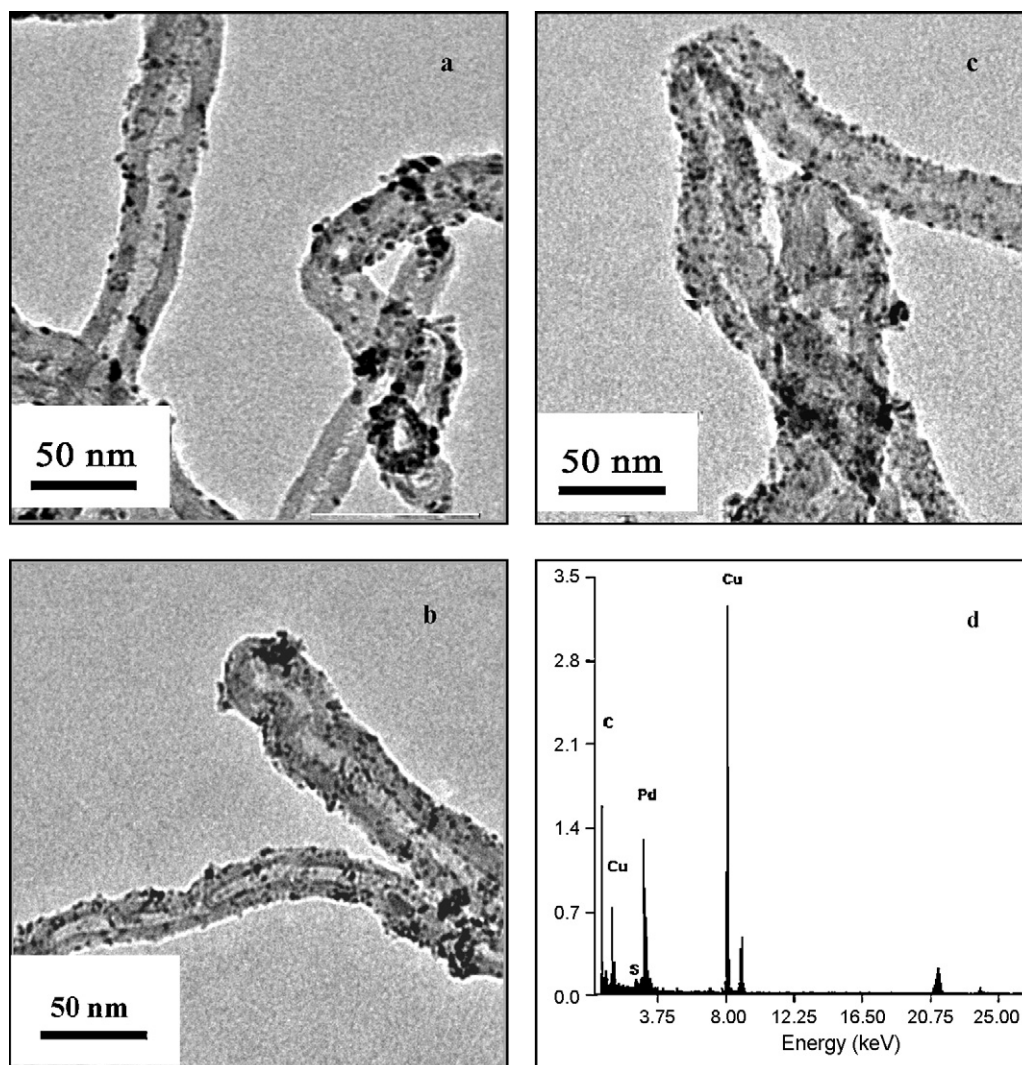

Fig. 4. TEM images of three catalysts: (a) P-MWNTS/Pd, (b) F-MWNTS/Pd, (c) S-MWNTS/Pd; (d) EDX analysis of S-MWNTS/Pd.
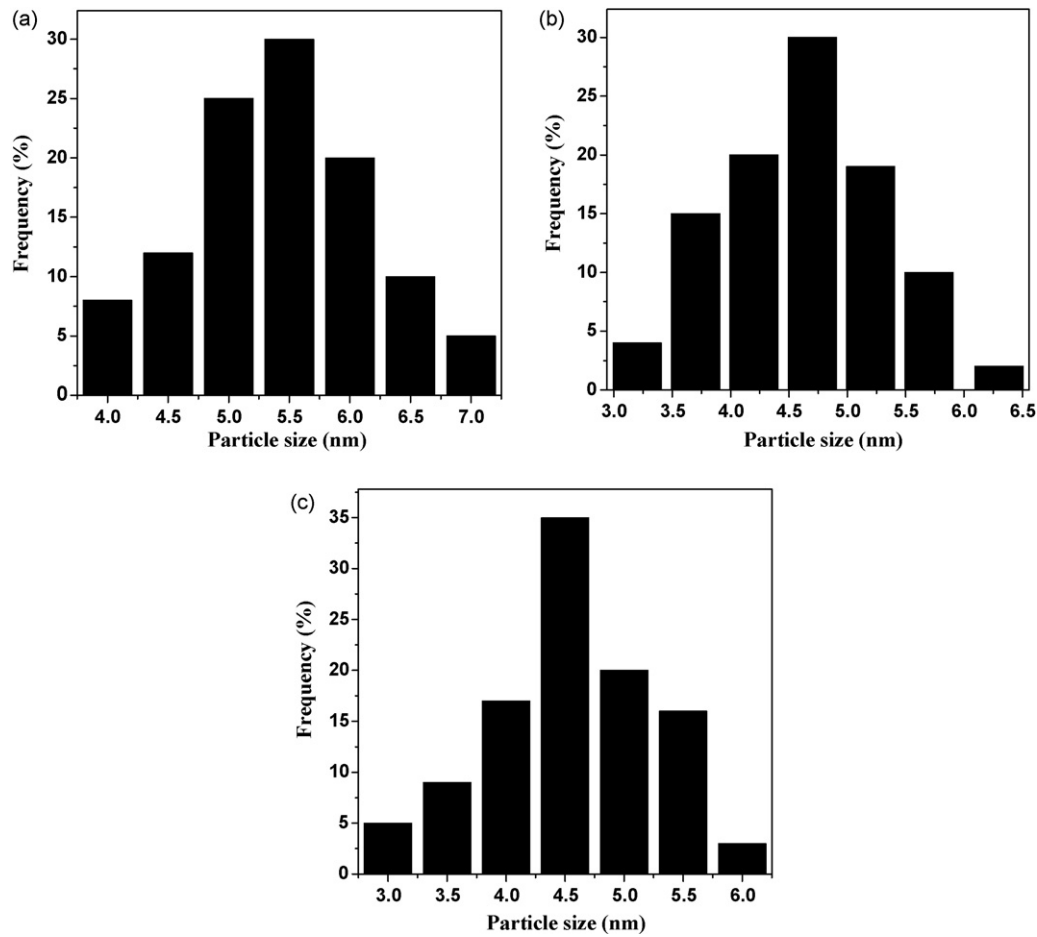
Fig. 5. Size distribution of Pd nanoparticles on: (a) P-MWNTS, (b) F-MWNTS, and (c) S-MWNTS.

is bigger than that of the P-MWNTS/Pd and F-MWNTS/Pd catalysts, as demonstrated in Fig. 6. The large electrochemically active surface area might be due to the high dispersion and small size of Pd nanoparticles on the S-MWNTS/Pd catalyst.

As shown in Fig. 7, the three catalysts displayed the similar feature, a typical EG 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 [4,9,29].

The current density of the F-MWNTS/Pd and P-MWNTS/Pd catalysts was 146.2 and 98.3 mA mg^{-1} Pd, respectively, while it was 177.2 mA mg^{-1} Pd in the case of S-MWNTs, almost twice of the P-MWNTS/Pd catalysts. In addition, the parameter of If/Ib value could be used to describe the catalyst tolerance to carbonaceous species accumulation [8,29]. The If/Ib value for P-MWNTs/Pd, F-MWNTs/Pd and S-MWNTs/Pd were 1.04, 1.30 and 1.94, respectively. A lower
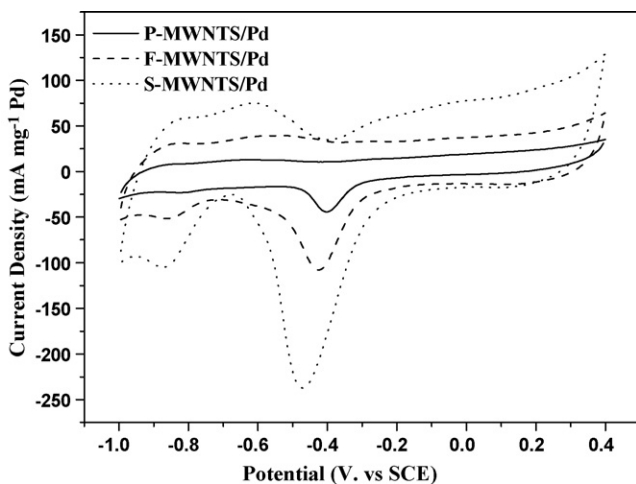

Fig. 6. Cyclic voltammograms of three catalysts in 0.2 M KOH aqueous solution (scan rate: 50 mV s^{-1}).
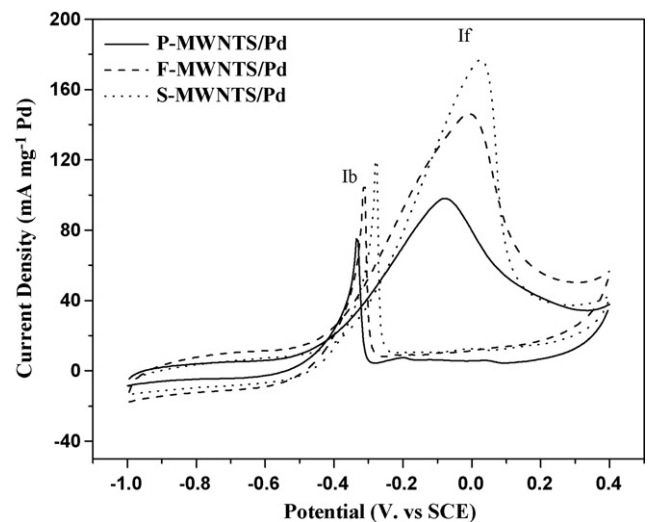

Fig. 7. Cyclic voltammograms of three catalysts in 0.2 M KOH aqueous solution containing 0.5 M EG (scan rate: 30 mV s^{-1}).
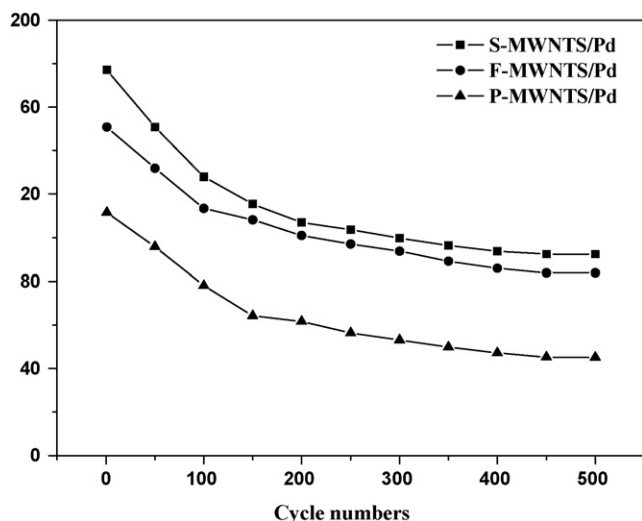
Fig. 8. Long-term stability of three catalysts in 0.2 M KOH aqueous solution containing 0.5 M EG (scan rate: 30 mV s^{-1}).

If/Ib value indicated 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 [9,30,31]. It could be seen that S-MWCNTs/Pd catalysts had the highest If/Ib ratio, indicating the best CO resistance among three catalysts.

Long-term stability of these catalysts was also investigated in 0.2 M KOH aqueous solution containing 0.5 M EG. It could be observed in Fig. 8 that the current densities of three catalysts decreased gradually with successive scans. However, the current density on S-MWNTs/Pd was found to higher than the other two catalysts in the whole process indicating that the S-MWNTS/Pd had good durability and stability towards EG electro-oxidation.

Based on the above results, the S-MWNTS/Pd catalysts presented the best electrocatalytic activity and stability towards EG oxidation among three Pd-based catalysts. The reasons might be explained as follows: (a) owing to the same loadings of Pd on the carbon supports, S-MWNTs/Pd had the smallest size of Pd nanoparticles, as a result, leading to the largest number of Pd particles involved in the electrochemical reactions, contributed to the best electrocatalytic activity [26,32]; (b) the specific electrostatic interactions between negatively charged MWNTs and positively charged Pd^{2+} could avoid the problems of aggregation and non-uniform size distribution of Pd nanoparticles associated with direct deposition of Pd at the defects. Furthermore, such novel interactions improved the stability of Pd particles on these MWNTs [8,25]; (c) the special frameworks and properties of S-MWCNTs/Pd hybrids were helpful to facilitate the transport of the electrolyte onto the surface of the catalysts and thus reduced the liquid sealing effect, which would enhance the active surface area for electrochemical reactions [5,29,33].

4. Conclusions

In summary, novel sulfonated-MWNTS derived from concentrated sulfuric acid and acetic anhydride through a facile synthesis route was employed as the carbon support for Pd catalysts. The homogeneously dispersed Pd nanoparticles supported on the novel carbon support were synthesized by a NaBH$_4$-assisted reduction. S-MWNTS/Pd catalysts had the best electrocatalytic activities and cyclic stability for EG electro-oxidation in contrast to the unsulfonated and traditional sulfonated counterparts. This novel approach is generally facile to implement and thus an attractive choice for large-scale sulfonate functionalization of CNTs, opening up enormous opportunities for CNTs-related technological applications.

References

[1] S.S. Fan, M.G. Chapline, N.R. Franklin, T.W. Tombler, A.M. Cassell, H.J. Dai, Science 283 (1999) 512.
[2] B. Wieland, J.P. Lancaster, C.S. Hoaglund, P. Holota, W.J. Tornquist, Langmuir 12 (1996) 2594–2610.
[3] C.A. Dyke, J.M. Tour, J. Am. Chem. Soc. 5 (2003) 1156–1159.
[4] Z.P. Sun, X.G. Zhang, Y.Y. Liang, H.L. Li, J. Power Sources 185 (2008) 801–806.
[5] S.Y. Wang, X. Wang, S.P. Jiang, Nanotechnology 19 (2008) 455602.
[6] H. Wang, Y. Zhao, Z. Jusys, R.J. Behm, J. Power Sources 155 (2006) 33–46.
[7] F. Ficicioglu, F. Kadirgan, J. Electroanal. Chem. 451 (1998) 95–99.
[8] V. Selvaraj, M. Alagar, Nanotechnology 19 (2008) 045504.
[9] M.S. Ureta-Zañartu, A. Alarcón, G. Muñoz, C. Gutiérrez, Electrochim. Acta 52 (2007) 7857–7864.
[10] G. Wu, Y.S. Chen, B.Q. Xu, Electrochem. Commun. 7 (2005) 1237–1243.
[11] Z.B. He, J.H. Chen, D.Y. Liu, H.H. Zhou, Y.F. Kuang, Diam. Relat. Mater. 13 (2004) 1764–1770.
[12] K. Jurkschat, S.J. Wilkins, C.J. Salter, H.C. Leventis, G.G. Wildgoose, L. Jiang, T.G.J. Jones, A. Crossley, R.G. Compton, Small 2 (2006) 95–98.
[13] K.H. An, W.S. Kim, Y.S. Park, J.M. Moon, D.J. Bae, S.C. Lim, Y.S. Lee, Y.H. Lee, Adv. Funct. Mater. 11 (2001) 387–392.
[14] J.L. Hudson, M.J. Casavant, J.M. Tour, J. Am. Chem. Soc. 126 (2004) 11158–11159.
[15] A. Eitan, K.Y. Jiang, D. Dukes, R. Andrew, L.S. Schadler, Chem. Mater. 15 (2003) 3198–3201.
[16] J.L. Bahr, J.M. Tour, Mater. Chem. 12 (2002) 1952–1958.
[17] C.C. Chen, C.F. Chen, C.M. Chen, F.T. Chuang, Electrochem. Commun. 9 (2007) 159–163.
[18] E.T. Mickelson, I.W. Chiang, J.L. Zimmerman, P.J. Boul, J. Lozano, J. Liu, R.E. Smalley, R.H. Hauge, J.L. Margrave, J. Phys. Chem. B 103 (1999) 4318–4322.
[19] Z.W. Zhao, Z.P. Guo, J. Ding, D. Wexler, Z.F. Ma, D.Y. Zhang, H.K. Liu, Electrochem. Commun. 8 (2006) 245–250.
[20] F. Peng, L. Zhang, H.J. Wang, P. Lv, H. Yu, Carbon 43 (2005) 2405–2408.
[21] M.M. Waje, X. Wang, W.Z. Li, Y.S. Yan, Nanotechnology 16 (2005) S395–S400.
[22] S.D. Yang, X.G. Zhang, H.Y. Mi, X.G. Ye, J. Power Sources 175 (2008) 26–32.
[23] Y.B. Wang, Z. Iqbal, S. Mitra, J. Am. Chem. Soc. 128 (2006) 95–99.
[24] B.S. Marietta, Sulfonated carbonaceous materials, US Patent 7,241,334 (2007).
[25] D.J. Guo, H.L. Li, J. Electroanal. Chem. 573 (2004) 197–202.
[26] C.Y. Du, T.S. Zhao, Z.X. Liang, J. Power Sources 176 (2008) 9–15.
[27] Y. Wang, F. Wei, G.H. Luo, H. Yu, G.S. Gu, Chem. Phys. Lett. 364 (2002) 568–572.
[28] H.J. Wang, H. Yu, F. Peng, P. Lv, Electrochem. Commun. 8 (2006) 499–504.
[29] C.W. Xu, L.Q. Cheng, P.K. Shen, Y.L. Liu, Electrochem. Commun. 9 (2007) 997–1001.
[30] C.W. Xu, Y.L. Liu, D.S. Yuan, Int. J. Electrochem. Sci. 2 (2007) 674–680.
[31] M.S. Ureta-Zanartu, A. Alarcon, G. Munoz, C. Gutierrez, Electrochim. Acta 52 (2007) 7857–7864.
[32] J.A. Kim, D.G. Seong, T.J. Kang, J.R. Youn, Carbon 44 (2006) 1898–1905.
[33] Z.P. Guo, D.M. Han, D. Wexler, R. Zeng, H.K. Liu, Electrochim. Acta 53 (2008) 6410–6416.