Research Article

In Situ Synthesis and Characterization of Polyethyleneimine-Modified Carbon Nanotubes Supported PtRu Electrocatalyst for Methanol Oxidation

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PtRu bimetallic nanoparticles were successfully synthesized on polyethyleneimine- (PEI-) functionalized multiwalled carbon nanotubes (MWCNTs) via an effective and facile polyol reduction approach. Noncovalent surface modification of MWCNTs with PEI was confirmed by FTIR and zeta potential measurements. The morphology, crystalline structure, and composition of the hybrid material were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray powder diffraction (XRD), and energy dispersive X-ray spectroscopy (EDX), respectively. According to SEM and TEM observations, PtRu nanoparticles with narrow size distribution were homogeneously deposited on PEI-MWCNTs. Cyclic voltammetry tests demonstrated that the as-prepared PtRu/PEI-MWCNTs nanocomposite had a large electrochemical surface area and exhibited enhanced electrocatalytic activity towards methanol oxidation in comparison with oxidized MWCNTs as catalyst support. PEI-functionalized CNTs, as useful building blocks for the assembly of Pt-based electrocatalyst, may have great potential for applications such as direct methanol fuel cell (DMFC).

1. Introduction

Over the past decade, carbon nanotubes (CNTs) with large active surface areas, excellent electronic conductivity, and high chemical stability have drawn considerable attention as an advanced supporting material for Pt-based catalysts [1, 2]. Nevertheless, the surface of pristine CNTs is chemically inert and hydrophobic, which is unfavorable for the deposition of metal nanoparticles (NPs) [3, 4]. For this reason, CNTs are usually pretreated with concentrated acid to introduce hydroxyl and carboxyl functional groups. On the one hand, these functional groups can improve the solubility of the CNTs and provide preferential sites for the immobilization of noble metal catalysts [5]. On the other hand, this common modification method will disrupt the graphite structure of CNTs and result in the loss of electrical conductivity and the reduction of corrosion resistance [6].

In general, there are two strategies involving the preparation of CNTs and nanoparticles (NPs) hybrids. In addition to the direct deposition of preprocessed NPs onto CNTs, CNTs surfaces can also be decorated by NPs via covalent or noncovalent bonds. With an attempt to overcome the defected structure and disruption of delocalized π electron systems caused by acid treatment, substantial efforts have been devoted to noncovalent functionalization of CNTs. As a versatile strategy, noncovalent functionalization of CNTs not only preserves the intrinsic structure of CNTs but also achieves the tailored properties of the nanocomposites (nanoworms, nanocubes, and nanoraspberries) [7–13]. Well-dispersed Pt nanoclusters on CNTs were prepared using bifunctional triphenylphosphine (PPh_3) or 1-aminopyrene (1-AP) as the interlinker, where the PPh_3 or 1-AP molecules were strongly adsorbed on the CNTs through noncovalent-stacking interaction and electrostatic

attractions [14–16]. CNTs modified by positively charged poly(diallyldimethylammonium chloride) (PDDA) have also been explored as templates for the deposition of Pt NPs with high density [17, 18]. By using polymer wrapping technique, a controllable decoration of CNTs with poly(sodium 4-styrenesulfonate) (PSS) and Pt NPs in sequence was described by Kongkanand et al. [19]. In addition, a novel route towards the self-assembly of cetyltrimethylammonium bromide (CTAB) stabilized Pt nanocubics on PSS modified CNTs has also been demonstrated by means of electrostatic interaction [20].

Polyethyleneimine (PEI), as a polymeric surfactant, has been investigated as an alternative to PDDA to achieve surface functionalization of noble metal NPs through coordination effects. Cationic PDDA has been extensively reported to achieve the surface functionalization of CNTs by endowing positive charges on the surface and may offer certain advantages. For example, it was suggested by previous studies that the permeability of small organic molecules may be larger in PEI films compared with PDDA films because PEI had random branched chains while PDDA chains may be more compact [21, 22]. Electrochemical study of different polyelectrolytes also observed different charge transfer behavior of linear and reticulated polyelectrolytes, with the former being considered as a linear chain of singly charged segment and the latter having more the characteristics of a multicharged ion [23]. Another study reported significant differences between the stabilizing efficiencies of PEI, PDDA, and poly(allylamine hydrochloride) (PAH) in synthesizing PbS nanoparticles and attributed the difference to their charge densities or their persistence lengths. Small monodispersed nanoparticles of PbS with a tight stabilizing shell were consistently found only when PEI was used [24].

Bai et al. presented a clean and efficient route to synthesize monodispersed Pt NPs via UV photoreduction of PEI mediated- PtCl_6^{2-} anions [25]. Cheng and Jiang prepared PEI-functionalized MWCNTs by microwave method, where PEI served as anchoring sites for PtRu nanoparticles' self-assembling [26]. PEI was also conducted as a stabilizing agent to synthesize water-soluble Pt 20–25 nm ranged dendrites in dimethylformamide (DMF) [27]. Moreover, the amino-rich PEI is known to be effectively attached on the sidewalls of CNTs via physisorption [28, 29]. Construction of one-dimensional CNTs/metal NPs (metal = Au, Pt, Pd, Ag) heterogeneous nanostructures has been shown via chemical reduction of PEI-metal ion complexes adsorbed onto CNTs [28, 30, 31].

In the pursuit of higher electrocatalytic activity and more stable performance, CNTs supported PtRu binary catalysts [32–34] have particularly been proven as the promising catalyst candidate for direct methanol fuel cell (DMFC). According to the bifunctional mechanism, the presence of Ru element could effectively modify the electronic nature of the Pt as well as remove the carbonaceous species to protect the Pt from being poisoned [35, 36]. To our knowledge, even though tremendous progress has been made to tailor the size and shape of Pt NPs on CNTs, little research work has been

conducted to control the morphology of bimetallic NPs by noncovalently functionalizing the surface of CNTs.

Herein, we present a simple and efficient synthesis route to anchor bimetallic PtRu electrocatalyst on PEI modified CNTs with tunable size and well-defined shape. Figure 1 illustrates the scheme of the immobilization of PtRu NPs on PEI-MWCNTs. The physiochemical and electrochemical properties of the as-prepared nanocomposites were characterized by zeta potential, FTIR, SEM, TEM, XRD, and cyclic voltammetry.

2. Experimental

2.1. Materials. Multiwalled carbon nanotubes (MWCNTs, 95% purity, diameter = 30 nm–60 nm) were obtained from Helix Material Solutions, Inc. Potassium tetrachloroplatinate (K_2PtCl_4 , 98%), ruthenium chloride (RuCl_3 , 98%), Nafion solution (5 wt% in ethanol), ethylene glycol (EG, 99%), and methanol (99%) were purchased from Sigma-Aldrich. Polyethyleneimine (PEI 50 wt% in water, $M_w = 60,000$), sulfuric acid (98 wt%), and nitric acid (69 wt%) were obtained from Alfa Aesar. All the chemicals were used as received without further purification. Ultrapure Milli-Q water (resistivity > 18.2 M Ω cm) was exclusively used for making aqueous solutions and rinsing procedures.

2.2. PEI and Acid Functionalization of MWCNTs. Noncovalent functionalization of MWCNTs by PEI was carried out through a procedure adapted from literature [28, 31]. Briefly, 100 mg of MWCNTs was dispersed in 200 mL 1 wt% PEI aqueous solution, followed by ultrasonication for 3 h and magnetic stirring for 12 h. Then, the stable PEI-MWCNTs suspension was filtered using a 0.2 μm nylon filter membrane and rinsed to remove the excess PEI. MWCNTs were also functionalized by the conventional acid-oxidation method in which 100 mg of pristine MWCNTs was refluxed in a 4 M H_2SO_4 and 4 M HNO_3 mixture at 120°C for 4 h [37]. The obtained oxidized MWCNTs were washed with copious water, filtered, and dried at 70°C overnight.

2.3. Synthesis of MWCNTs Supported PtRu Electrocatalysts. PtRu/PEI-MWCNTs catalyst was prepared by an in situ polyol reduction method. The typical procedure is as follows: PEI-CNT was dispersed in an EG solution under ultrasonic treatment and vigorous agitation; calculated amount of K_2PtCl_4 and RuCl_3 with a molar ratio of Pt:Ru = 1:1 was added dropwise to achieve the nominal PtRu loading of 10 wt%, 30 wt%, and 50 wt%, respectively. The mixture was heated to 140°C and maintained for 3 h to completely reduce the metal precursors. A flow of ultrahigh purity nitrogen was also introduced to the reaction system to isolate oxygen and to remove organic byproducts during the synthesis step. After the deposition of PtRu NPs, the as-synthesized PtRu/PEI-MWCNTs hybrid material was centrifugalized, rinsed repeatedly, and dried overnight. For comparison purpose, oxidized MWCNTs supported PtRu nanocomposite (denoted as PtRu/O-MWCNTs) with Pt:Ru atomic ratio of 1:1 and 30 wt% metal loading was also prepared and collected [38].

FIGURE 1: Schematic of the synthesis of PtRu electrocatalyst on PEI-functionalized MWCNTs.

2.4. Physiochemical Characterization. To monitor the surface charge of MWCNTs, the zeta potential measurement was performed using a Malvern Zetasizer Nano ZS90. FTIR spectra were acquired by Bruker Optics Vetex70 spectrometer to further confirm the functionalization of MWCNTs with PEI. The morphology of the nanocomposite was studied by a JEOL 7000F scanning electron microscope (SEM) and JEOL 100CX (LaB₆ filament) transmission electron microscope (TEM) operating at an accelerating voltage of 100 kV. The presence of noble metal NPs is detected by energy dispersive X-ray analysis (EDX) and the X-ray diffraction (XRD) patterns of the samples were recorded using a Rigaku Geigerflex X-ray diffractometer with Cu K α radiation.

2.5. Electrochemical Analysis. Cyclic voltammetric measurements were carried out on a BASi 100B electrochemical analyzer with a conventional three-electrode cell. Glassy carbon electrode (GCE) (3 mm in diameter) was used as the working electrode, on which a thin layer of Nafion-impregnated PtRu/MWCNTs catalyst was applied. The catalyst loading was fixed at 1 mg/cm² for both the 30 wt% PtRu/PEI-MWCNTs and 30 wt% PtRu/O-MWCNTs modified GCE electrodes. Platinum wire served as the counter electrode and Ag/AgCl electrode was used as the reference electrode. The electrochemical active surface area (ECSA) was calculated using cyclic voltammograms of the nanocomposite catalyst in the solution of 0.5 M H₂SO₄. The electrocatalytic activity for the methanol oxidation was characterized by cyclic voltammetry (CV) in a solution of 1 M CH₃OH + 0.5 M H₂SO₄. The electrolyte solution was deaerated with ultrahigh purity N₂ prior to the measurement and the entire experiment was conducted at room temperature.

3. Results and Discussion

3.1. Zeta Potential Measurement of PEI-MWCNTs Nanocomposite. Zeta potential is the electrical potential existing at the shear plane of a nanoparticle, which has been widely used to determine the surface charge at the electric double layer [18]. During the measurement, low concentration samples (0.01 wt%) were dispersed in 1 mM NaCl solutions to ensure the constant ionic strength. The pH of the suspension was adjusted by adding either HCl or NaOH [18, 39]. The zeta potential as a function of pH for pristine and PEI-treated MWCNTs is shown in Figure 2. The pristine MWCNTs have a low isoelectric point (pH_{IEP}) at 4.9, whereas the pH_{IEP} moves to a more basic value at 8.1 after being treated by PEI. This result indicates that the cationic PEI polymer chains are noncovalently attached onto the MWCNTs surface. PEI are reported to form PEI-metal ion complexes with several metal compounds such as K₂PdCl₄, K₂PtCl₄ [31], AgNO₃ [40], and CuCl₂ [41]. Hence, it is hypothesized that the positively charged amine groups of PEI could act as the anchor sites for the PtCl₄²⁻ anions, followed by the electrostatic attraction of Ru³⁺ cations. In situ reduction of these noble metal precursors will facilitate the uniform dispersion of PtRu NPs on MWCNTs.

3.2. FTIR Spectra Analysis of PEI-Functionalized MWCNTs. The FTIR spectra of pristine MWCNTs and PEI-MWCNTs are shown in Figure 3. Three weak peaks at 1225 cm⁻¹, 1578 cm⁻¹, and 1630 cm⁻¹ (marked by blue asterisks) reveal the graphite structure of pristine MWCNTs [42]. By comparison, one sharper adsorption peak at 1637 cm⁻¹ (marked by red asterisks) is identified on the spectrum of PEI-MWCNTs,

FIGURE 2: Zeta potential as a function of pH for pristine MWCNTs and PEI-MWCNTs.

which can be assigned to the bending vibration of N–H [37, 42, 43]. These results verify the successful noncovalent modification of MWCNTs with PEI.

3.3. Morphology of PtRu NPs Decorated on PEI-MWCNTs and O-MWCNTs. Figure 4 shows the representative TEM micrographs and the corresponding particle size distribution histograms of the as-prepared electrocatalysts. In the case of 30 wt% PtRu/O-MWCNTs (Figure 4(a)), the PtRu NPs are mainly distributed in the range of 2 to 8 nm and the mean particle size is estimated to be 4.3 nm using Gaussian fit (Figure 4(b)). Poor dispersion and obvious aggregation of PtRu nanocrystals on O-MWCNTs are observed, which is consistent with previous reports [18, 44, 45]. The formation of the agglomeration can be elucidated by the strong tendency of PtRu NPs to nucleate on the localized defect sites introduced by the harsh oxidation process. By contrast, PtRu NPs are homogeneously deposited on the external walls of PEI modified MWCNTs (Figures 4(c), 4(e), and 4(g)). For 10 wt% PtRu loading, the NPs with the mean size of 2.6 nm are distinctively isolated from each other and sparsely dispersed on the surface of PEI-MWCNTs (Figure 4(d)). The particle size increases to 3.1 nm for 30 wt% PtRu/PEI-MWCNTs due to the existence of a small amount of nanoclusters. Despite the fact that the homogeneous coverage is still maintained on 50 wt% PEI-MWCNTs (Figure 4), further increment in PtRu loading density gives rise to a continuous nanosheath structure, where almost all the NPs are interconnected with each other with the resulting particle size of 3.8 nm on average. The relatively small particle size and narrow size distribution is probably attributed to the presence of PEI coating, providing abundant adsorption sites for PtRu precursors, thereby realizing the uniform assembly of metal NPs. Moreover, PEI may also serve as an effective stabilizer to isolate the adjacent noble metal nanocrystals from coalescence [25, 46].

FIGURE 3: FTIR spectra of pristine MWCNTs and PEI-coated MWCNTs.

As shown in the SEM images (Figure 5(b)), PtRu NPs are evenly immobilized on PEI-MWCNTs. According to EDX analysis (Figure 6), the atomic ratio of Pt to Ru is almost 1 : 1, while the total PtRu loading is approximate to 30 wt%, which is close to the initial feed ratio. For the sample with 10 wt% and 50 wt% PtRu loading, we also obtained very consistent results. It is evident that the noble metal loading can be readily controlled by altering the concentration of the precursors.

3.4. X-Ray Diffraction Patterns of PtRu/MWCNTs Nanocomposites. The X-ray diffractograms of pristine MWCNTs, PtRu/PEI-MWCNTs, and PtRu/O-MWCNTs nanocomposites are shown in Figure 7. The diffraction peaks at around 26.3° , 43.0° , 54.3° , and 79.8° correspond to (002), (100), (004), and (110) of the graphite structures of MWCNTs. Although the acid oxidation procedures usually have detrimental effects on the graphene structure of MWCNTs, the graphite peaks of the oxidized MWCNT seem to be slightly higher than PEI modified MWCNT. This phenomenon can be explained by the physisorption of a thin layer of amorphous PEI coating on the surface of MWCNT, which causes attenuation of the graphite peak intensity in XRD pattern. The diffraction peaks for PtRu/O-MWCNTs at around 40.5° , 47.5° , 68.7° , and 81.8° can be indexed to (111), (200), (220), and (311) crystalline planes of FCC (face-centered cubic) Pt, which shifted to high angle value with respect to pure FCC Pt (PDF card 4-802). This trend of peak displacements was also found for the PtRu/PEI-MWCNTs electrocatalyst with different PtRu loading, which implies the formation of PtRu alloy resulting from the incorporation of smaller Ru atoms into Pt phase [47, 48]. Since the standard reduction potentials of $\text{PtCl}_4^{2-}/\text{Pt}$ and Ru^{3+}/Ru are 0.758 V and 0.704 V (versus SHE) [49], respectively, there is a strong likelihood that the metal precursors were simultaneously reduced to PtRu alloy nanoparticles. In addition, no hcp Ru phase was identified on the XRD pattern, which further verified the formation of

(a)

(b)

(c)

(d)

(e)

(f)

FIGURE 4: Continued.

FIGURE 4: TEM images and the corresponding PtRu particle size distribution histograms of 30 wt% PtRu/O-MWCNTs ((a), (b)); 10 wt% PtRu/PEI-MWCNTs ((c), (d)); 30 wt% PtRu/PEI-MWCNTs ((e), (f)); and 50 wt% PtRu/PEI-MWCNTs ((g), (h)).

FIGURE 5: SEM images of pristine MWCNTs (a), 30 wt% PtRu/PEI-MWCNTs (b).

FIGURE 6: EDX spectrum of 30 wt% PtRu/PEI-MWCNTs.

bimetallic PtRu alloy rather than the separate phases of Pt and Ru NPs. According to the Scherer equation

$$d = \frac{0.9\lambda_{K\alpha}}{B_{2\theta} \cdot \cos \theta}, \quad (1)$$

where d is the average particle size of PtRu NPs (nm), $\lambda_{K\alpha}$ is wavelength of X-ray ($\lambda_{K\alpha} = 0.15406 \text{ nm}$), θ is the peak angle, and $B_{2\theta}$ is the full width half maximum in radians, the mean PtRu particle sizes are estimated to be 2.9 and 4.0 nm for 30 wt% PtRu/PEI-MWCNTs and 30 wt% PtRu/O-MWCNTs using the broadening of isolated (220) peak [50]. These results are in good agreement with TEM observations.

3.5. The Electrochemical Surface Area of the Nanocomposite Electrocatalyst. The hydrogen electrosorption voltammograms for 30 wt% PtRu/PEI-MWCNTs and 30 wt% PtRu/O-MWCNTs electrocatalysts are shown in Figure 8. The characteristic peak in the region of -0.2 V to 0.1 V can be attributed to atomic hydrogen adsorption on the Pt surface. And the ECSA for the catalysts can be estimated by the following equation:

$$\text{ECSA} = \frac{Q}{q^0 \times M_{\text{Pt}}}, \quad (2)$$

where Q is the integrated area of the hydrogen desorption (μC), q^0 is the charge for monolayer hydrogen adsorption

FIGURE 7: XRD patterns of pristine MWCNTs, 30 wt% PtRu/PEI-MWCNTs, and 30 wt% PtRu/O-MWCNTs.

FIGURE 8: Cyclic voltammograms of PtRu (30 wt% loading) supported on PEI-MWCNTs and O-MWCNTs in 0.5 M H₂SO₄ at a scan rate of 50 mV/s (the current densities are normalized by geometric surface area of the modified glassy carbon electrode).

on Pt, $q^0 = 210 \text{ C} \cdot \text{cm}^{-2}$, a value generally admitted for polycrystalline Pt electrodes [51], and M_{Pt} is the mass of the Pt loading.

It is found that the PtRu/PEI-MWCNTs catalysts exhibit large ECSA around $81.7 \text{ m}^2/\text{g}_{\text{Pt}}$ compared with $60.9 \text{ m}^2/\text{g}_{\text{Pt}}$ for PtRu/O-MWCNTs. The larger ECSA of PtRu/PEI-MWCNTs implies that more catalyst sites are accessible for electrochemical reactions, which can be attributed to the small particle size and high dispersion of PtRu NPs. Furthermore, it may also suggest that PEI coating on MWCNTs effectively prevent the PtRu nanoclusters from agglomeration and thus promote the electrocatalytic activity [25].

Since the ECSA alone cannot exactly represent the utilization efficiency of the noble metal, it is also necessary to investigate how many surface atoms are contributing to

the electrochemical reactions. Thus, the ratio of ECSA to the geometrical specific surface areas (S_{geom}) can be considered as an important indicator to evaluate the Pt utilization efficiency [52, 53]. Here, the S_{geom} can be calculated by

$$S_{\text{geom}} = \frac{6000}{\rho d}, \quad (3)$$

$$\rho_{\text{PtRu}} = X_{\text{Pt}}\rho_{\text{Pt}} + X_{\text{Ru}}\rho_{\text{Ru}},$$

where d (nm) is the mean particle diameter, ρ (g/cm^3) is the density of NPs, X is the weight fraction of metal, $\rho_{\text{Pt}} = 21.4 \text{ g}/\text{cm}^3$, and $\rho_{\text{Ru}} = 12.3 \text{ g}/\text{cm}^3$ [48, 50].

For 30 wt% PtRu/O-MWCNTs, the S_{geom} and the utilization ratio are estimated to be $76.3 \text{ m}^2/\text{g}$ and 79.8%, respectively. It is interesting to find that the S_{geom} is $105.8 \text{ m}^2/\text{g}$ and the resulting utilization ratio is 77.2% for 30 wt% PtRu/PEI-MWCNTs. Similar utilization efficiency for both catalysts suggests that the methanol accessibility to the active sites of PtRu electrocatalyst will not be impeded by PEI coating on MWCNTs.

3.6. Electrocatalytic Activity of PtRu/MWCNTs towards Methanol Oxidation. Figure 9 illustrates the CV profiles of the electrocatalysts in $1 \text{ M CH}_3\text{OH} + 0.5 \text{ M H}_2\text{SO}_4$. In the forward sweep, the featured methanol oxidation peaks are observed at approximately 0.70 V for 30 wt% PtRu/PEI-MWCNTs and 30 wt% PtRu/O-MWCNTs. In the reverse scan, the anodic peak at 0.47 V is mainly associated with the removal of the residue carbonaceous species [54]. In principle, the onset potential of methanol oxidation is related to the breaking of C–H bonds and the subsequent removal of intermediates such as CO_{ads} by oxidation with OH_{ads} species supplied by Ru–OH sites [6, 55]. Both the catalysts have comparable onset potential of methanol electrooxidation (MEO) at 0.3 V or so. This result indicates that the noncovalent modification of MWCNTs with PEI will not block the charge transfer during the electrocatalysis, and MEO is energetically favorable on the PtRu/PEI-MWCNTs nanocomposite. In addition, it is also worthwhile to note that the peak current density during the forward scan is $65.4 \text{ mA}/\text{cm}^2$ for PtRu/PEI-MWCNTs, almost 1.4 times as large as that of PtRu/O-MWCNTs. This number is also higher than the commercial PtRu/C catalyst with current density of $17.4 \text{ mA}/\text{cm}^2$ in sweep rate 50 mV/s [56]. The significant improvement in the catalytic activity for MEO is most likely due to the high ECSA of the former catalyst.

3.7. Long-Term Durability of PtRu/MWCNTs towards Methanol Oxidation. The stabilities of 30 wt% PtRu/PEI-MWCNTs and 30 wt% PtRu/O-MWCNTs electrocatalysts towards MEO were examined by potential cycling between -0.2 V and 1 V (versus Ag/AgCl) in $1 \text{ M CH}_3\text{OH} + 0.5 \text{ M H}_2\text{SO}_4$. As shown in Figure 10, the forward peak current density (I_f) increases initially and reaches the maximum value after 40 cycles for both electrocatalysts and it is followed by a gradual decay of I_f during the successive CV scans. Using the peak current density measured after 40 cycles

FIGURE 9: Cyclic voltammograms of PtRu (30 wt% loading) supported on PEI-MWCNTs and O-MWCNTs in 0.5 M H_2SO_4 + 1 M CH_3OH at a scan rate of 50 mV/s (the current densities are normalized by geometric surface area of the modified glassy carbon electrode).

FIGURE 10: Long-term stability of PtRu (30 wt% loading) supported on PEI-MWCNTs and O-MWCNTs in 0.5 M H_2SO_4 + 1 M CH_3OH at a scan rate of 50 mV/s.

(I_0) as the reference, the anodic peak current density (I_f) is about 55% of I_0 for 30 wt% PtRu/PEI-MWCNTs after CV scanning for 500 cycles, whereas the ratio of I_f/I_0 is only 42% for 30 wt% PtRu/O-MWCNTs. In general, the loss of catalytic activity with the increase of cycles may result from methanol consumption, increase in catalyst particles size, and accumulation of poisoning carbonaceous species on the electrode surface [57]. In comparison with PtRu/O-MWCNTs, the relatively higher ratio of I_f/I_0 indicates that PtRu/PEI-MWCNTs are more durable for electrooxidation of methanol. The enhanced durability is probably associated

with the homogeneous dispersion of uniform-sized PtRu nanoparticles on PEI-MWCNTs support, which could effectively mitigate the catalyst coarsening during the long-term potential cycling. A detailed and statistically meaningful study comparing the morphology of PtRu catalyst system before and after cycling is undergoing and will be presented in our next paper.

4. Conclusions

In summary, we presented an efficient and novel method to tether PtRu bimetallic NPs on the surface of PEI modified MWCNTs. Compared with the conventional acid-oxidization procedure, noncovalent functionalization of MWCNTs with PEI preserved the integrity of graphite structure and favored the uniform dispersion of PtRu NPs. The CV characterizations demonstrated that PtRu/PEI-MWCNTs nanocomposite exhibited superior electrocatalytic performance, which might be a promising anode catalyst for DMFCs.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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