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纳米三氧化钨复合催化剂的制备及对甲醇电催化性能

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摘要: 采用浸渍沉淀法制备出 WO₃-碳纳米管(WO₃-CNTs)纳米复合材料, 微波辅助乙二醇法在其表面负载活性成分 Pt, 得到纳米 Pt/WO₃-CNTs 催化剂. 采用 X 射线衍射(XRD), 透射电子显微镜(TEM)和 X 射线光电子能谱(XPS)等测试手段对催化剂的结构和形貌进行表征, 结果表明 Pt 纳米粒子为面心立方晶体结构, 粒径大小在 3–5 nm 之间, 均匀地分布在 WO₃-CNTs 纳米复合材料表面, 同时发现催化剂中的 Pt 主要以金属态的形式存在. 采用循环伏安和计时电流法研究了在酸性溶液中 Pt/WO₃-CNTs 催化剂对甲醇的电催化氧化性能, 结果表明 Pt/WO₃-CNTs 催化剂比用硝酸处理的碳纳米管载铂催化剂(Pt/CNTs)对甲醇呈现出更高的电催化氧化活性和抗 CO 中毒性能.

关键词: 直接甲醇燃料电池; 碳纳米管; 三氧化钨; 电催化

中图分类号: O646

Nano-WO₃ Composite Materials as Electro-Catalyst for Methanol Oxidation

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Abstract: Nano-WO₃ modified carbon nanotube supported Pt nanoparticles (Pt/WO₃-CNTs) with uniform dimension were prepared by impregnated precipitation method, and Pt nanoparticles were loaded on the surface of WO₃-CNTs by means of microwave-assisted glycol method. X-ray powder diffraction (XRD) and transmission electron microscopy (TEM) reveal that the Pt nanoparticles have a face-centered cubic crystal structure and are highly dispersed on the surface of WO₃-modified CNTs with a narrow size distribution between 3 and 5 nm. X-ray photoelectron spectroscopy (XPS) shows that more metallic Pt is present on Pt/WO₃-CNTs than on Pt/CNTs catalyst. Compared with the Pt/CNTs catalyst without WO₃ modification, the Pt/WO₃-CNTs composite catalyst not only shows relative large electrochemical active surface area, high catalyst activity toward methanol electro-oxidation, but also exhibits very high stability with apparent antiposition tolerance to the incomplete oxidized species during methanol oxidation.

Key Words: Direct methanol fuel cell; Carbon nanotube; Tungsten trioxide; Electro-catalysis

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1 Introduction

Direct methanol fuel cells (DMFCs) have recently attracted considerable attentions due to their excellent features such as high-energy density, convenient fuel storage, green emission, and ambient operating conditions etc.^{1,2} However, DMFCs usually use lots of expensive platinum as anodic catalysts that tend to be poisoned by reaction intermediates such as CO_{ads}.³ Thus considerable efforts have been devoted to making metallic alloy, such as PtRu,^{4,5} PtPd,^{6,7} and PtRuSn^{8,9} etc., with low amount of platinum and high activity toward methanol oxidation. But the dissolution of transition metals in the alloys during the DMFC operation would be the main challenge since the dissolved transition metals may span the membrane and experience reduction on the cathode, finally leading to the unexpected performance degradation of DMFCs.^{10,11}

The second way to design Pt-based composite catalysts is metal oxides modified Pt particles, such as Pt/RuO₂,^{12,13} Pt/SnO₂,^{14,15} and Pt/MnO₂,¹⁶ etc. Tungsten trioxide (WO₃) is known to be able to form a hydrogen tungsten bronze (H_xWO₃) compound in acid solution which is both nonstoichiometric and electrically conducting. The compound can facilitate dehydrogenation during methanol oxidation and lighten the CO poisoning of Pt catalyst. Previous studies have shown that Pt and PtRu catalysts supported on WO₃ have extremely high activity towards the electro-oxidation of CO,¹⁷ methanol,^{18–21} ethanol,²² and formic acid.^{23,24} However, WO₃ has a low specific surface area and conductivity, which limits its application in DMFC.

Recently WO₃/C hybrid material was used as the support of Pt-WO₃/C catalysts.^{25,26} Compared with Vulcan XC-72 carbon black, carbon nanotubes (CNTs) have better specific surface area and conductivity. Rajesh *et al.*²⁷ reported a composite catalyst of methanol electro-oxidation by depositing Pt nanoparticles on WO₃-modified CNT, in which CNT was synthesised by the template carbonisation of polypyrrole on alumina membrane. In this paper CNT was further disposed by strong acid so that Pt and WO₃ nanoparticles were homogeneously deposited on the surface of CNT. Results show that WO₃-modification improves significantly electrocatalytic activity towards methanol oxidation.

2 Experimental

2.1 Preparation of WO₃ modified acid treated CNTs

Carbon nanotubes (Shenzhen Nanoharbor Co., China) were functionalized in nitric acid (65%–68%) under refluxing at 150 °C for 5 h, washed by distilled water and dried in vacuum at 85 °C.²⁸ WO₃-modified carbon nanotubes (WO₃-CNTs) were prepared by the conventional means with sodium tungstate as the precursor. Briefly, 50 mg of CNTs was added into 5 mmol·L⁻¹ aqueous solution of sodium tungstate. After ultrasonic dispersed for 30 min, the solution were stirred vigorously at 60 °C for 1 h, then excessive 1 mol·L⁻¹ hydrochloric acid was drop-wised into the above solution. After the reaction proceeded for 6 h, the suspension was filtered, washed and dried at 80 °C in a

vacuum oven. The resultant was transferred into a tubular oven and heat-treated at 500 °C for 6 h under the protection of a nitrogen atmosphere. The ideal ratio of WO₃ to CNTs was calculated as 25% (w), but for comparison, ratio of WO₃ to CNTs with 10%, 25%, 50%, and 75% (w) were also prepared following same procedures as above.

2.2 Synthesis of Pt nanoparticles on WO₃-CNTs

Platinum supported on the WO₃-modified CNTs (Pt/WO₃-CNTs) was prepared by means of microwave heating ethylene glycol method. In brief, 5.7 mL of 5 mmol·L⁻¹ chloroplatinic acid was well mixed with 15 mL ethylene glycol (EG) in a special reaction tube, and then 50.0 mg of as-prepared WO₃/CNTs was added into the mixture. After the pH of the mixture was adjusted to 10 using 1.0 mol·L⁻¹ NaOH aqueous, well-dispersed slurry was obtained after being stirred in an ultrasonic bath for 30 min. Thereafter, the slurry was microwave-heated at 160 °C for 30 min in the microwave synthesizer (Initiator Biotage, Sweden). The resulting solution was filtered, washed and dried at 85 °C for 10 h in a vacuum oven, yielding 10% (w) Pt loading on the supports. As contrast samples, Pt nanoparticles (10% (w) metal content) on acid treated CNTs (Pt/CNTs) was prepared using similar procedures as described above.

2.3 Characterizations

The morphology, crystal phase, structure and element distribution of the samples were respectively characterized by XRD, XPS, and TEM. XRD was performed with a Thermo ARL SCINTAG X'TRA X-ray at room temperature, using quartz monochromatic Cu K_{α1} radiation source (λ=0.1541 nm) under a voltage of 45 kV and a current of 40 mA. The XRD patterns were recorded with a step size of 0.04° from 10° to 80° at the speed of 2.4 (°)·min⁻¹. TEM was carried out on a Tecnai G2 F30 S-Twin (Philips-FEI). XPS was carried out on Kratos AX-IS Ultra DLD.

2.4 Electrochemical measurements

Electrochemical measurements were performed on Ivium electrochemical workstation. A standard three-electrode cell with separate anode and cathode compartments was used. A Pt foil and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. For electrode preparation, 2.5 mg of electrocatalyst sample was ultrasonically mixed in 400 μL of ethanol-water solution (1:1, V/V) to form a homogeneous ink followed by dropping 5 μL of the electrocatalyst ink onto the surface of a glassy carbon electrode (GCE, with a diameter of 3 mm), and 7 μL of Nafion solution of 1.0% (DuPont, USA) in ethanol was added to fix the electrocatalyst on the GCE surface. The electrochemical active surface (EAS) assessed in a nitrogen-saturated 0.5 mol·L⁻¹ H₂SO₄ solution at a scan rate of 50 mV·s⁻¹ and the electrocatalytic activity for the methanol oxidation reaction was measured in a nitrogen-saturated 0.5 mol·L⁻¹ H₂SO₄+1.0 mol·L⁻¹ CH₃OH solution at a scan rate of 50 mV·s⁻¹.

The CO stripping experiments were performed in a 0.5 mol·L⁻¹ H₂SO₄ solution. Along with the continuous CO bubbling for

30 min, the anode electrode was controlled at -0.14 V for CO adsorption. The solution was then purged with N₂ for 30 min to remove the dissolved CO before the stripping test.

3 Results and discussion

3.1 XRD and TEM analysis of samples

Fig.1 shows the typical XRD patterns of the samples. The diffraction peak at $2\theta=26.2^\circ$ is characteristic of the graphite (002) plane, demonstrating the graphitization of carbon in the sample. The distinct diffraction peaks at 2θ of 23.09° , 23.58° , 24.33° , 33.25° , 34.12° , and 41.44° are indexed as the (002), (020), (200), (022), (202), and (222) planes of monoclinic WO₃ phase.²⁹ Those slight diffraction peaks at 2θ of 39.76° , 46.28° , and 67.53° are attributed to the Pt (111), (200), and (220) planes, which are not obvious for Pt/WO₃-CNTs, indeed, the broaden peak centered at 41.45° is the overlapped peak of the (111) peak of Pt and the (222) peak of WO₃.

Fig.2 shows scanning transmission electron microscope

Fig.1 XRD patterns of (a) WO₃-CNTs, (b) Pt/WO₃-CNTs, and (c) Pt/CNTs catalysts

(STEM) images of Pt/CNTs and Pt/WO₃-CNTs catalyst. The black and white picture is sample particle morphology and color pictures are samples' elements distribution density by energy dispersive spectrometer (EDS) surface scan. As can be seen from Fig.2(a), W, Pt, and O elements are distributed on the outer surface of CNTs. Combined with XRD characterization of results, Pt/WO₃-CNTs catalyst is composed of Pt, WO₃, and CNTs.

Fig.3 gives the TEM images of Pt/CNTs and Pt/WO₃-CNTs catalysts and the corresponding histograms of the Pt particle diameters, as well. It can be seen from the TEM images that the Pt particles on the WO₃-CNTs support are smaller and more uniformly dispersed than those on CNTs support. The average sizes of the Pt particles in Pt/CNTs and Pt/WO₃-CNTs catalysts are estimated from their histograms as being approximately 4.8 and 3.6 nm, respectively, indicating that the introduction of WO₃ can inhibit the aggregation of Pt particles.²⁶

3.2 XPS analysis of samples

Fig.4 shows the XPS spectra of Pt 4f and W 4f photoemission from Pt/WO₃-CNTs, respectively. The two characteristic peaks observed in the Pt 4f region with binding energies of 71.5 and 74.8 eV should be attributed to the metallic Pt.³⁰ The two peaks in the W 4f region with binding energies centered at 35.7 and 37.9 eV, suggest the presence of tungsten in the +VI oxidation state.³¹ Fig.5 displays the XPS spectra of Pt 4f photoemission from Pt/CNTs. It can be observed that the two peaks with binding energies of 71.5 and 74.8 eV are characteristic of the metallic Pt, and the other two peaks at 72.3 and 75.8 eV can be assigned to Pt²⁺ in PtO and Pt(OH)₂-like species.³²

3.3 Electro-catalytic performance

Fig.6 presents cyclic voltammograms (CVs) of Pt/CNTs and Pt/WO₃-CNTs in 0.5 mol·L⁻¹ H₂SO₄ solution at a scan rate of 50 mV·s⁻¹. The platinum in Pt/WO₃-CNT has a larger EAS

Fig.2 EDS elemental mapping of (a) Pt/WO₃-CNTs and (b) Pt/CNTs catalysts under STEM model

Fig.3 TEM images of (a) Pt/WO₃-CNTs and (b) Pt/CNTs, and Pt particle size distributions of (c) Pt/WO₃-CNTs and (d) Pt/CNTs

Fig.4 XPS spectra of the Pt 4f and W 4f photoemission from Pt/WO₃-CNTs

than that in Pt/CNTs, which is reflected by the hydrogen adsorption/desorption currents at the potentials between -0.2 and 0.2 V, as shown in Fig.6. The EAS of platinum can be calculated from the integrated charge in the hydrogen adsorption region of the cyclic voltammograms (Fig.6) based on $ESA = Q_H / 0.21 \times [Pt]$, where Q_H is the integrated charge (mC), $[Pt]$ is the Pt loading ($\text{mg} \cdot \text{cm}^{-2}$) on the electrode. The EAS values calculated for Pt/CNTs and Pt/WO₃-CNTs are shown in Table 1, which reveals that the EAS of platinum is influenced by the particle sizes. This result is consistent with Pt particle size distributions of Pt/CNTs and Pt/WO₃-CNTs (Fig.3).

Fig.7 shows CVs of the electrodes in $0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4 + 1 \text{ mol} \cdot \text{L}^{-1} \text{CH}_3\text{OH}$ solution between 0.0 to 1.0 V at a scan rate of

$50 \text{ mV} \cdot \text{s}^{-1}$. The electrocatalytic activity of Pt/WO₃-CNTs and Pt/CNTs catalysts on the oxidation of methanol was studied in $0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$ aqueous solution containing $1.0 \text{ mol} \cdot \text{L}^{-1} \text{CH}_3\text{OH}$ at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$. It can be observed from Fig.7 that the onset of methanol oxidation peaks for the Pt/WO₃-CNTs catalyst is at 0.25 V, which is apparently lower than that on Pt/CNTs catalysts with the onsets at 0.30 V. The negative shift on the potential onset of Pt/WO₃-CNTs indicates that Pt nanoparticles on WO₃-CNTs surface can effectively reduce the over potentials in the methanol electro-oxidation reaction. In addition, it can be seen that the mass specific current of Pt/WO₃-CNTs ($403 \text{ mA} \cdot \text{mg}^{-1}$) is 5 times that of Pt/CNT ($80 \text{ mA} \cdot \text{mg}^{-1}$) at 0.69 V, indicating that WO₃ plays a key role in

Fig.5 XPS spectra of the Pt 4f photoemission from Pt/CNTs

Fig.6 Cyclic voltammograms of (a) Pt/WO₃-CNTs and (b) Pt/CNTs in 0.5 mol·L⁻¹ H₂SO₄ solution at a scan rate of 50 mV·s⁻¹

Table 1 Onset potential, EAS, peak current density, and forward anodic to reverse anodic peak current density ratio of the different catalysts for methanol oxidation

Catalyst	Onset potential/mV	EAS/(m ² ·g ⁻¹)	<i>I</i> _{max} /(mA·mg ⁻¹)	<i>I</i> _f / <i>I</i> _b
Pt/WO ₃ -CNTs	0.25	26.0	403	1.37
Pt/CNTs	0.30	13.4	80	0.96

the high catalytic performance.

Besides, it is well known that the ratio of the forward anodic peak current density (*I*_f) to the reverse anodic peak current density (*I*_b), i.e., *I*_f/*I*_b, suggests a tolerance to carbonaceous species accumulation of catalysts during methanol electro-oxidation. And the high *I*_f/*I*_b indicates excellent oxidation of methanol during the reverse anodic scan and less accumulation of residues on the catalyst. Here the *I*_f/*I*_b ratio for Pt/WO₃-CNT is about 1.37, which is much higher than that of Pt/CNT catalyst (0.96), showing the Pt/WO₃-CNT has a better tolerance to carbonaceous species accumulation.

Fig.8(a) shows the cyclic voltammograms of Pt/WO₃-CNTs catalyst with different mass contents of WO₃ in 0.5 mol·L⁻¹ H₂SO₄+1.0 mol·L⁻¹ CH₃OH solution. In Fig.8(b), the effects of WO₃ content on the anodic peak current density and the *I*_f/*I*_b ratio are shown. It can be seen that for Pt/WO₃-CNTs catalyst, the peak current density of methanol oxidation increases along with the increasing of WO₃ content because WO₃ reduces the Pt nanoparticles size and improves the dispersion of Pt nanoparticles on the surface of CNTs.²⁶ However, the increas-

Fig.7 Cyclic voltammograms of methanol oxidation on (a) Pt/WO₃-CNTs, (b) Pt/CNTs, and (c) WO₃/CNTs in 0.5 mol·L⁻¹ H₂SO₄+1 mol·L⁻¹ CH₃OH solution at a scan rate of 50 mV·s⁻¹

Fig.8 (a) Cyclic voltammograms of the Pt/WO₃-CNTs catalyst with different mass contents of WO₃ in 0.5 mol·L⁻¹ H₂SO₄+1.0 mol·L⁻¹ CH₃OH solution with a scan rate of 50 mV·s⁻¹; (b) dependency of anodic peak current density and the ratio of *I*_f/*I*_b to the mass fraction of WO₃

ing of WO₃ amount would lead to a decrease of the electrode conductivity, thus decreases the reaction performance of Pt/WO₃-CNTs catalyst on the contrary, finally, the content of WO₃ is optimized at ca 25%.

CO-stripping voltammograms is measured and the characteristic CO stripping curves of Pt/WO₃-CNTs and Pt/CNTs catalysts are shown in Fig.9. The onset potential and the peak potential may directly reflect the CO oxidizing ability of the catalysts. It is revealed that the onset potential and the peak potential for the oxidation of adsorbed CO on Pt/WO₃-CNTs (Fig.9 (a)) are much lower than those on Pt/CNTs (Fig.9(b)), so WO₃

Fig.9 CO-stripping voltammograms of Pt/WO₃-CNTs and Pt/CNTs catalysts in 0.5 mol·L⁻¹ H₂SO₄ solution at room temperature and a scan rate of 50 mV·s⁻¹

Fig.10 Chronoamperometric curve of Pt/CNTs and Pt/WO₃-CNTs in 0.5 mol·L⁻¹ H₂SO₄+1 mol·L⁻¹ CH₃OH solution at an operation potential of 0.7 V

efficiently reduces the overpotential of CO oxidation due to forming H_xWO₃-OH_{ads} species at lower potentials, which is helpful to oxidize CO_{ads} through bi-functional mechanism.³³

The chronoamperometry (CA) curves for the three catalysts are shown in Fig.10. These curves reflect the activity and stability of the catalysts to catalyze methanol oxidation. Obviously, the decay in the methanol oxidation current with time varies. But after 100 min the current density of Pt/WO₃-CNTs catalyst is 15 times higher than that of Pt/CNTs catalyst. It shows that the modification of WO₃ can effectively improve the resistance to toxic and stability of Pt-based catalyst for methanol oxidation. This significant improvement in the catalytic performance of the Pt/WO₃-CNTs catalysts may be attributed to three factors: first, the Pt and WO₃ particles supported on the carbon are smaller and more uniformly distributed; second, more metallic Pt is present on Pt/WO₃-CNTs than on Pt/CNTs catalyst. Third, in the presence of WO₃, the hydrogen adsorbed on the Pt spills over onto the surface of the WO₃ and forms H_xWO₃, thus releasing these Pt active sites. Subsequently, H_xWO₃ can be readily oxidized to release hydrogen ions, electrons, and WO₃.^{34,35} This cyclic process will accelerate the dehydrogenation of methanol on Pt and improve the catalytic performance of meth-

anol oxidation. The cyclic process on the Pt/WO₃-CNTs catalyst is speculated to occur as follows:^{33,34}

4 Conclusions

Nano-WO₃ modified carbon nanotubes were prepared by the conventional means with sodium tungstate as the precursor. Platinum supported on the WO₃-modified CNTs (Pt/WO₃-CNTs) was prepared by means of microwave heating ethylene glycol method. Electrochemical analysis shows that the Pt/WO₃-CNTs catalysts prepared exhibit excellent catalytic activity and stability for methanol electro-oxidation.

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