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Pd Nanoparticles Supported on PDDA-Functionalized Ti_4O_7 as an Effective Catalyst for Formic Acid Electrooxidation

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Pd catalysts supported on carbon black and Ti_4O_7 were prepared and used as electrocatalysts for formic acid electrooxidation. The structure and morphology were characterized by XRD and TEM. CV results show that $\text{Pd}/\text{Ti}_4\text{O}_7$ possesses a higher catalytic activity than Pd/C . XPS analyzes suggest that the higher content of metallic Pd caused by Ti_4O_7 contributes to the better catalytic performance. Based on the good electrocatalytic performance of $\text{Pd}/\text{Ti}_4\text{O}_7$, Pd catalyst supported on PDDA-functionalized Ti_4O_7 was prepared and exhibited a better catalytic activity. The improvement results from the further increase of metallic Pd content due to the presence of PDDA.

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Direct formic acid fuel cells (DFAFCs) have attracted growing attention in recent years as promising clean power sources due to their advantages, such as relatively low fuel toxicity, high electromotive force, high energy density and low fuel crossover through a Nafion membrane.^{1,2} Among various metal electrocatalysts for formic acid oxidation, palladium has been regarded as the most popular one.³ Unfortunately, the electrochemical activity of Pd catalyst for formic acid oxidation still needs to be further enhanced before DFAFC can be employed for practical application.

In addition to metal electrocatalysts, support materials of electrocatalysts are also very important for the performance of DFAFCs.⁴ Carbon black is a commonly used support in fuel cells. However, the corrosion of the carbon support would cause a negative impact on the working efficiency and performance of fuel cells.⁵ Recently, titanium-based oxides have received considerable attention owing to their strong catalyst-support interaction as well as high corrosion resistance.^{6,7} Among these oxides, Ti_4O_7 has been found to be a promising support material with higher corrosion resistance and superior electrical conductivity than carbon black.⁷ Some Ti_4O_7 supported catalysts showed good electrochemical performance and excellent CO-tolerance in hydrogen oxidation reaction.^{8,9} However, the electrocatalytic properties of Pd supported on Ti_4O_7 for formic acid oxidation have not been reported so far.

Additionally, non-covalent functionalization has been proposed as a promising approach to alter catalyst-support interaction, because it enables attachment of molecules or charged polyelectrolytes onto support through van der Waals forces or π - π interaction.^{10,11} For example, Poly(diallyldimethylammonium chloride) (PDDA), as an effective ionic polyelectrolyte, has been successfully used in electrostatic assembly of metal nanoparticles on carbon nanotube surfaces.¹² However, to the best of our knowledge, the performance of PDDA-functionalized Ti_4O_7 as a catalyst support in DFAFCs has not been reported yet. In this work, Ti_4O_7 was functionalized with PDDA, and it was found that Pd nanoparticles deposited on the PDDA-functionalized Ti_4O_7 have a significantly higher activity for formic acid electrooxidation reaction compared to Pd nanoparticles deposited on carbon black and Ti_4O_7 supports. This work provides a new way to construct anode electrocatalyst for DFAFCs.

Experimental

The chemicals used in this work were carbon black (Vulcan XC-72), poly(diallyldimethylammonium chloride) (PDDA, 20 wt% in water, MW = 100,000–200,000, Aldrich-Sigma), PdCl_2 , $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, NaBH_4 , H_2SO_4 , HCOOH , Nafion solution

(5 wt% in isopropanol and water) and deionized water. Ti_4O_7 was purchased from ShanDong Lianmeng Chemical Group Co. LTD.

PDDA-functionalized Ti_4O_7 was prepared as follows: 100 mg Ti_4O_7 was dispersed into a 250 mL beaker containing a PDDA solution (0.5 wt%, 100 mL). Then the suspension was stirred overnight and the final product was obtained through filtration and drying under 60°C. The functionalized Ti_4O_7 was denoted as PDDA- Ti_4O_7 .

To synthesize the electrocatalysts, 100 mg support materials including carbon black, Ti_4O_7 , PDDA- Ti_4O_7 were added into 75 mL deionized water and sonicated for 8 min, respectively. Then 41.7 mg PdCl_2 and 103.7 mg $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ were added into above suspensions. Afterwards, excess amount of 0.01 M NaBH_4 aqueous solution (freshly prepared) was added dropwise, followed by stirring for 6 hours at room temperature. Finally, the suspensions were filtered and washed several times with deionized water, and the remaining solids were dried at 60°C overnight. The catalysts were harvested and denoted as Pd/C , $\text{Pd}/\text{Ti}_4\text{O}_7$ and $\text{Pd}/\text{PDDA-Ti}_4\text{O}_7$. The theoretical content of Pd is 20 wt%.

Structure and morphology of the catalysts were investigated by X-ray diffraction (XRD, Smartlab (9 kw), Cu $\text{K}\alpha$) and transmission electron microscopy (TEM, JEM-2100, 200 kV). X-Ray photoelectron spectroscopy (XPS) characterization was carried out on an ESCALAB 250Xi (Thermo Fisher Scientific Inc.) spectrometer using an Al $\text{K}\alpha$ source.

The electrochemical measurements were conducted on an electrochemical workstation system (CHI760D, Chenhua, Shanghai) with a three-electrode cell using Pt foil and saturated calomel electrode (SCE) as the counter and reference electrodes, respectively. Cyclic voltammetry (CV) was performed in a 0.5 M H_2SO_4 + 0.5 M HCOOH solution, where oxygen was removed by purging N_2 for 15 min. The working electrode was prepared by dropping 5 μL of the electrocatalyst ink onto glassy carbon electrode (GCE). The ink was prepared by ultrasonically mixing 4 mg electrocatalyst sample in 2 mL of ethanol for 8 min. Then 1 μL of Nafion solution was dropped on top to fix the electrocatalysts. All potentials in this work were given versus SCE electrode (+0.241 V vs. NHE). The CV experiments were conducted at a sweep rate of 50 mV s^{-1} , with potentials ranging from -0.2 V to 1.0 V. CO stripping was performed as follows: after purging the solution with N_2 for 20 min, gaseous CO was bubbled for 15 min to form a CO adlayer on catalysts while maintaining potential at 0.1 V. Excess CO in solution was purged with N_2 for 20 min, and CO stripping voltammetry was recorded in 0.5 M H_2SO_4 at 20 mV s^{-1} .

Results and Discussion

XRD patterns of the Pd/C and $\text{Pd}/\text{Ti}_4\text{O}_7$ catalysts are shown in Fig. 1a. There are four diffraction peaks corresponding to (111), (200),

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Figure 1. (a) XRD patterns of Pd/C and Pd/Ti₄O₇; TEM images of (b) Pd/C and (c) Pd/Ti₄O₇, inset: histograms of particle size distribution for Pd/C and Pd/Ti₄O₇; (d) CVs of Pd/C and Pd/Ti₄O₇ in a 0.5 M H₂SO₄ + 0.5 M HCOOH solution.

(220) and (311) planes of Pd at ca. 40, 46, 68 and 81°, respectively.^{12,13} The diffraction peak at ca. 25° in the pattern of Pd/C belongs to the characteristic peak of carbon.¹³ For Pd/Ti₄O₇, other peaks except Pd peaks are well matched with the characteristic peaks of Ti₄O₇ (PDF (The Powder Diffraction File): 50-0787). Fig. 1b and 1c present TEM images of the Pd/C and Pd/Ti₄O₇ catalysts. It can be seen that metal nanoparticles are dispersed uniformly on the support materials. According to the measurements for the sizes of sixty particles, the average sizes of metal particles in Pd/C and Pd/Ti₄O₇ are calculated to be 2.88 and 3.11 nm, respectively. The insets in Fig. 1b and 1c provide the histograms of particle size distribution. Fig. 1d shows the CVs of formic acid electrooxidation on the Pd/C and Pd/Ti₄O₇ catalysts. The specific mass activity of Pd/Ti₄O₇ is about 1.4 times as large as that of Pd/C. It indicates that the Pd/Ti₄O₇ catalyst has better electrocatalytic performance than the Pd/C catalyst.

To further improve the catalytic performance, Ti₄O₇ was functionalized with PDDA. Fig. 2a presents the XPS spectra of PDDA-Ti₄O₇ support material. It can be clearly seen that the characteristic N 1s peak was recorded at about 400 eV, suggesting that Ti₄O₇ was successfully functionalized by PDDA. Fig. 2b shows the XRD pattern of the Pd/PDDA-Ti₄O₇ catalyst. The characteristic diffraction peaks of Pd and Ti₄O₇ are in agreement with those corresponding peaks in the pattern of Pd/Ti₄O₇ (shown in Fig. 1a). Fig. 2c presents the TEM image of Pd/PDDA-Ti₄O₇, and the inset provides the histogram

of particle size distribution. The average size of metal particles is 3.23 nm. Compared to Pd/C and Pd/Ti₄O₇, it can be seen that the distribution of metal nanoparticles in Pd/PDDA-Ti₄O₇ is more homogeneous. The improvement of dispersion status results from the self-assembly process of nanoparticles on PDDA-functionalized Ti₄O₇.¹⁴ Fig. 2d displays the CVs of the Pd/PDDA-Ti₄O₇ catalyst measured in a 0.5 M H₂SO₄ + 0.5 M HCOOH solution. For comparison, the CVs of the Pd/Ti₄O₇ catalyst are also presented in this figure. The specific mass activity of Pd/PDDA-Ti₄O₇ is about 1.4 times as large as that of Pd/Ti₄O₇ and the peak potential of the former is about 0.019 V more negative than that of the latter. This demonstrates that Pd/PDDA-Ti₄O₇ possesses better catalytic activity.

To understand the effect of the supports on electronic properties of catalysts, Pd 3d core level spectra of the Pd/C, Pd/Ti₄O₇ and Pd/PDDA-Ti₄O₇ catalysts were recorded in Fig. 3. The binding energies of all peaks are referenced to C 1s value of 284.6 eV. The Pd 3d signals of Pd/PDDA-Ti₄O₇ were fitted by two pairs of overlapping Lorentzian curves (Fig. 3c), and the more intense peaks (335.6 and 340.8 eV) can be attributed to metallic palladium, Pd(0). The second set of doublets (336.5 and 341.8 eV) can be attributed to the Pd(II) chemical state on PdO or Pd(OH)₂. The Pd 3d XPS spectra of Pd/C and Pd/Ti₄O₇ (Fig. 3a and 3b) are similar to those of Pd/PDDA-Ti₄O₇. However, the relative intensity of metallic Pd(0) in Pd/PDDA-Ti₄O₇ is 70.0%, much higher than 61.9 and 33.4% obtained for Pd/Ti₄O₇

Figure 2. (a) XPS spectra of PDDA-Ti₄O₇; (b) XRD pattern of Pd/PDDA-Ti₄O₇; (c) TEM image of Pd/PDDA-Ti₄O₇, inset: histogram of particle size distribution for Pd/PDDA-Ti₄O₇; (d) CVs of Pd/PDDA-Ti₄O₇ and Pd/Ti₄O₇ in a 0.5 M H₂SO₄ + 0.5 M HCOOH solution.

Figure 3. XPS spectra of Pd (3d) for (a) Pd/C, (b) Pd/Ti₄O₇ and (c) Pd/PDDA-Ti₄O₇; (d) CO stripping curves on these three catalysts recorded in 0.5 M H₂SO₄ solution.

Table I. Binding energy and relative intensity of XPS spectra of Pd species in the Pd/PDDA-Ti₄O₇, Pd/Ti₄O₇ and Pd/C catalysts.

Catalysts	Species	Binding energy of Pd 3d _{5/2} (eV)	Binding energy of Pd 3d _{3/2} (eV)	Relative intensity (%)
Pd/PDDA-Ti ₄ O ₇	Pd(0)	335.60	340.85	70.01
	Pd(II)	336.53	341.77	29.99
Pd/Ti ₄ O ₇	Pd(0)	335.72	340.97	61.92
	Pd(II)	336.65	341.87	38.08
Pd/C	Pd(0)	335.99	341.25	33.41
	Pd(II)	336.90	342.18	66.59

and Pd/C, respectively. Accordingly, the relative intensity of Pd(II) decreases gradually in the sequence of Pd/C, Pd/Ti₄O₇ and Pd/PDDA-Ti₄O₇. Table I lists the binding energies and relative intensity of Pd(0) and Pd(II) of three catalysts evaluated from XPS analyzes. The higher metallic content of Pd on Ti₄O₇ compared to that on carbon black indicates the “metallization” effect of the Ti₄O₇ support. This effect can be ascribed to the electrostatic interaction between metal particles and supports. Because the valence electron configuration of Ti is 3d²4s², Ti₄O₇ is an oxygen deficit species, namely betatopic configuration. Thus, some electrons of Ti₄O₇ may have a tendency to transfer to Pd, leading to an increase of metallic palladium content. It is well known that the higher the content of metallic state in catalysts, the better the catalytic performance.^{15,16} Therefore, the higher content of Pd(0) caused by the Ti₄O₇ support contributes to the better catalytic activity of Pd/Ti₄O₇ than that of Pd/C. For Pd/PDDA-Ti₄O₇, because PDDA is a positively charged ionic polymer,¹⁷ an electrostatic inductive effect in the preparation process of the PDDA-functionalized Ti₄O₇ supported catalyst will lead to a further increase in the content of metallic Pd,¹² which results in the better catalytic performance than Pd/Ti₄O₇.

In order to further investigate the electrocatalytic performance of these three catalysts toward formic acid oxidation, CO stripping curves were collected, as shown in Fig. 3d. It can be seen that the onset potentials of CO oxidation on these three catalysts are similar. This means that the promoting effect of the Ti₄O₇ and PDDA-Ti₄O₇ supports cannot be explained by a bi-functional mechanism.¹⁸ According to the XPS analyzes mentioned above, this effect is mainly ascribed to the modification of electronic solid state properties of metal particles.

Conclusions

The Pd/C and Pd/Ti₄O₇ catalysts were prepared and their catalytic performance for formic acid electrooxidation was compared. It was found that Pd/Ti₄O₇ possesses better electrocatalytic activity. The analysis for XPS spectra indicates that the higher content of metallic Pd caused by the Ti₄O₇ support contributes to the better catalytic activity of Pd/Ti₄O₇. Based on the good performance of Pd/Ti₄O₇, the

Pd/PDDA-Ti₄O₇ catalyst was synthesized and showed better catalytic activity than Pd/Ti₄O₇. The improvement is attributed to the further increase of metallic Pd content due to the presence of PDDA.

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