High activity of novel Pd/TiO$_2$ nanotube catalysts for methanol electro-oxidation

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Abstract

Electro-oxidation of methanol in sulfuric acid solution was studied using palladium well-dispersed on titanium nanotubes, in relation to methanol oxidation processes in the direct oxidation methanol fuel cell. Pd dispersed on titania nanotubes, which leads to high surface area substrates, showed excellent catalytic activities compared to those of pure Pd and Pd–TiO$_2$ nanoparticles. TEM results show a narrow distribution of TiO$_2$ nanoparticles whose particle size is about 10 nm, and uniform nano-sized TiO$_2$ nanotubes with 10 nm in diameters are seen from HRTEM . A homogeneous structure in the composite nanomaterials is indicated by XRD analysis. The composite electrode activities were measured by cyclic voltammetry (CV) and at 25 °C it was found that 3 wt% Pd in titania nanotubes had the best activity for methanol oxidation.
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Keywords: Palladium nanoparticles; TiO$_2$ nanotubes; Methanol electro-oxidation

1. Introduction

Direct methanol fuel cells (DMFCs) show great promise as high-efficiency, low-emission future power sources. The performance of DMFCs has improved markedly in the past several years to approach that of decades-optimized reformate-fed fuel cells. High activity of methanol oxidation on platinum makes this metal a suitable electrocatalyst for the DMFCs anode. However, It has been conclusively shown that Pt could affect the anode activity by greatly poisoning CO. Numerous attempts are underway on the addition of Ru or any other metal to Pt, which could improve the activity of the catalysts [1–5]. In fact, as a noble metal too, palladium is much cheaper than platinum, and if it has the same activity for methanol electro-oxidation, which has been proved in our work, Pd may have a promising future.

Electrodes based on dispersed noble metal on an inert high area substrates are one of the workhorse of electrochemical technology [6]. TiO$_2$ nanofilm electrode has been the hotspot because of its special photoelectric and electric properties [7,8]. In addition, TiO$_2$ is stable in acidic or alkaline solutions, which has shown high activity of catalyst for the reduction of some small organic molecules [9]. It has been reported that TiO$_2$ electrode as the base of platinum changed the electronic property of the Pt surface just because there was some strong effect between TiO$_2$ and Pt, as a result of which the chemistry adsorption on the surface was faint [10]. Liu et al. also reported there was some cooperative effect for platinum catalyst in the existence of TiO$_2$, which made CO absorbed oxidate rapidly [11]. In the previous paper, it was shown that spraying a suspension of titanium surface, followed by thermal treatments in air and in high vacuum, leads to a uniform, nanos-tructured titanium dioxide layer with high porosity and surface area [12].

In this paper, these titanium nanotubes are employed as substrates for palladium. The titanium nanotubes

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were obtained through a hydrothermal route from titanium dioxide nanoparticles preproducts [13]. With TiO_2 nanotubes being the substrates, $PdCl_2$ was reduced to Pd by ethenyl glycol in the oil bath at $120\,°C$.

Palladium dispersed on titania nanotubes with high surface-to-volume ratios was the most effective catalyst compared with the TiO_2 particles or the pure palladium as the substrates. Comparing different ratios of Pd/TiO_2 nanotubes, 3 wt% palladium has the best activity due to its the most catalytic activity points in the process of methanol oxidation. All products were testified using transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), cyclic voltammetry (CV), EDS, and X-ray diffraction (XRD). TEM indicated that the TiO_2 particles were around 10 nm in size and the nanotubes were less than 10 nm in diameter. It has been proved that Pd/TiO_2 nanotube composites could be the hopeful catalysts with their superior activities in the direct oxidation methanol fuel cells (DMFCs).

2. Experimental

2.1. Preparation of TiO_2 nanoparticles

The nanoparticles were prepared by the sol–gel method as given in Ref. [14]. In the typical reaction, 6 mL acetic acid solution mixed with 20 mL distilled water and 20 mL ethanol was dropped in the solution containing 7.2 mL $Ti(OBu)_4$ (or 4 mL $TiCl_4$) and 80 mL ethanol. The ethanol/H_2O ratio was controlled between 4:1 and 5:1. The precipitation was direct at $80\,°C$ for 4 h to remove the water and the ethanol, then placed in the muffle annealing at $500\,°C$ for 2 h and cooled to room temperature.

2.2. Preparation of TiO_2 nanotubes

The mixture of 0.8 g obtained TiO_2 nanoparticles in 15 mL 10 M NaOH solution was ultrasonicated and placed in a Teflon-lined stainless-steel autoclave at $120\,°C$ for 24 h, then cooled to room temperature. After that the as-prepared products were treated with 0.1 M HCl , washed with distilled water, and purified.

2.3. Preparation of well-dispersed Pd/TiO_2 nanotube electrocatalysts

Pd-based catalysts were synthesized at $120\,°C$ using the conventional reduction method with glycol. TiO_2 nanotubes were mixed with glycol and $PdCl_2$ in Millipore water ($18\,M\Omega\,cm$) until they dispersed well. The Pd salt was reduced by glycol under constant stirring. The resulting material was washed with deionized water and dried by vacuum drying.

2.4. Characterization of catalysts

Composite catalysts were dispersed in Nafion ethanol solution. The solution was sonicated for 15 min, and then the catalyst solution was applied by a micropipet to the titanium electrode surface, which was polished with 1, 0.3, and $0.05\,\mu m$ Al_2O_3 paste and washed ultrasonically in Millipore water, and dried. Electrochemical measurements were made using a three-electrode cell at $25\,°C$. Pt foil and SCE were used as the counter and reference electrodes, respectively. The titanium electrode was the working electrode which was brushed with the catalyst ink as described previously [4]. All potentials are reported vs SCE in the paper. Solution of 1 M H_2SO_4 and 1 M CH_3OH in 1 M H_2SO_4 were purged with N_2. Electrochemical experiments were performed by CHI 600 electrochemical workstation (Chenhua, Shanghai). To identify the properties of the Pd-based catalyst in H_2SO_4 and to measure the onset potential of methanol oxidation, CV was performed in the potential between -0.2 and $1.2\,V$.

The morphology of synthesized nanoparticles was observed on a Hitachi 600 transmission electron microscope (TEM). The samples were prepared by dropping TiO_2 nanomaterials ethanol solution on the Cu grids and were observed at 100 kV.

X-ray diffraction (XRD) data of the samples were collected using a Rigaku D/MAX 24000 diffractometer with CuKα radiation.

The elemental compositions of the Pd–TiO_2 composite were investigated by electron diffraction spectroscopy (EDS) (Vantage 4105, NORAN).

3. Results and discussion

3.1. TEM analysis of TiO_2 nanoparticles and TiO_2 nanotubes

In Fig. 1, the TEM images of the nanoparticles show that the diameters of TiO_2 hydrolyzed from $TiCl_4$ and $Ti(OBu)_4$ are about 10 nm (Fig. 1a) and 30 nm (Fig. 1b), respectively. Also, it can been seen that these particles have uniform morphologies and the phenomenon of reuniting is not visible. Fig. 1b shows that the nanoparticle size of TiO_2 is larger when $Ti(OBu)_4$ was the preproduct than then fabricated from $TiCl_4$, and the particles were dispersed better as shown in Fig. 1a.

Fig. 2 shows some high-resolution transmission electron microscopy (HRTEM) images of the typical nanotubes prepared by hydrothermal treatment of TiO_2 shown in Fig. 1. Most of the nanotubes are close ended. However, some open-ended nanotubes are observed occasionally. The nanotubes are made of mutilayered sheets. The outer diameter (OD) of the nanotubes is about 15 nm and the inner diameter (ID) of the
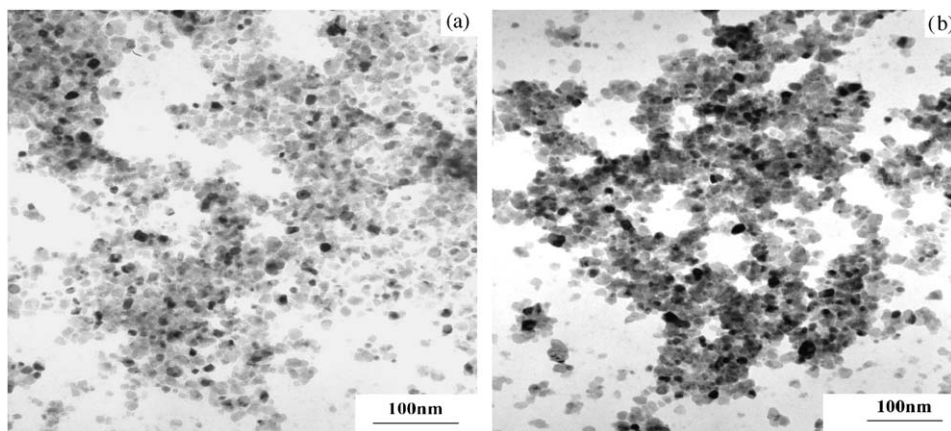
Fig. 1. TEM images of TiO$_2$ hydrolyzed from TiCl$_4$ (a) and Ti(OBu)$_4$ (b).
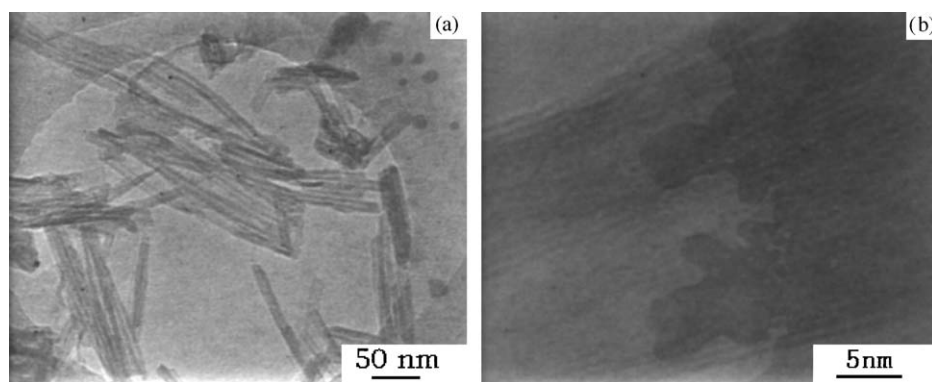

Fig. 2. High-resolution TEM images of TiO$_2$ nanotubes.

nanotube is about 10 nm. The interlayer spacing is about 3 nm. Various aspect ratios (the length of the tubes can be as long as a few hundred nanometers) and the excellent crystallization are noted. The single crystallinity of these nanotubes is unambiguously evidenced by the highly resolved TiO$_2$ lattice fringe details (see HRTEM images in Fig. 2), while their crystal structure is confirmed by the XRD method.

3.2. XRD pattern of TiO$_2$ and Pd–TiO$_2$ nanotubes

From the XRD pattern shown in Fig. 3a, the structures of the sample prepared by TiO$_2$ nanoparticles shown in Fig. 1(a) can be seen. This pattern shows a mixture containing not only anatase but also rutile structures. The diffraction (101) planes of anatase and the diffraction (110) of rutile in Fig. 3a is sharp and broadened indicating good crystallization and small size. From all the diffraction patterns it is also obvious that the materials are in the form of quite small-sized tubes, as the peaks are very broad. As confirmed in Fig. 3b the structure of anatase still existed, and the rutile crystalline remained too. It looks the same as in (a) except at $2\theta = 39.9378$, where the diffraction (111) of
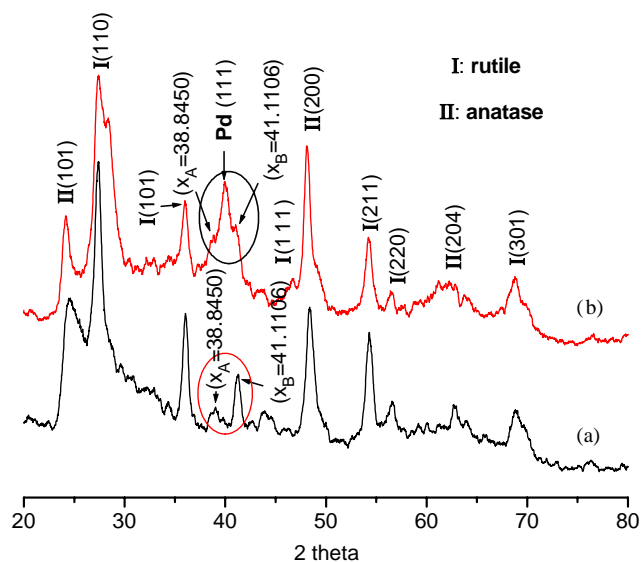

Fig. 3. XRD patterns for TiO$_2$ nanotubes prepared from TiO$_2$ (a) and Pd/TiO$_2$ nanotubes (b).

palladium nanoparticles was obviously observed in the pattern (b). It seems just one peak but actually three diffraction planes were testified (Fig. 3b). Two of the
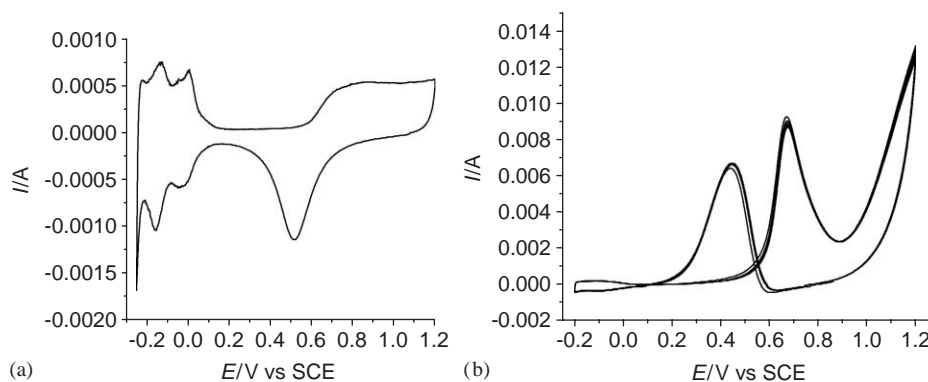
Fig. 4. (a) Cyclic voltammograms of the Pd–TiO$_2$ nanotube materials/titanium electrode in 1 M H$_2$SO$_4$ at room temperature at a scan rate of 50 mV/s. (b) CVs (50 mV/s) of Nafion-dispersed Pd–TiO$_2$ tube catalysts deposited on titanium electrode in 1 M CH$_3$OH + 1 M H$_2$SO$_4$.

peaks have the same positions in the *X*-axis in Fig. 3a ($X_A = X'_A = 38.8450$ and $X_B = X'_B = 41.1106$ which were coincided well with the diffraction (200) planes and the diffraction (111) planes of rutile, respectively). The patterns confined in the circle (Fig. 3b) look so broad due to the small size of Pd nanoparticles and TiO$_2$ nanotubes, which diffract each other, making it broaden.

3.3. Electrochemical performance of catalysts

Cyclic voltammograms (CVs) were collected for Pd–TiO$_2$ nanotubes electrocatalyst in nitrogen-purged 1 M H$_2$SO$_4$ (Fig. 4a), which is used to electrochemically characterize and stabilize the catalyst materials, before methanol oxidation was undertaken. In the case of Pd–TiO$_2$ nanotube materials, hydrogen adsorption/desorption peaks (H upd peaks) are seen centered at ca. -0.1 V; anodic current due to Pd oxide formation is also seen, commencing already at 0.7 V, with its reduction occurring in a peak at 0.5 V under these conditions.

Fig. 4b shows the first ten scan cyclic voltammograms for Pd-catalyzed TiO$_2$ nanotubes on Ti electrode in 1 M CH$_3$OH + 1 M H$_2$SO$_4$. On the first scan to positive potentials from -0.2 V, the onset of the methanol oxidation was around $+0.21$ V and a large methanol oxidation peak was observed at $+0.70$ V on the positive irreversible scan and another acute peak of methanol oxidation was seen at $+0.46$ V on the reverse scan. Formation of palladium oxide whose peak was observed on the scan at $+0.5$ V leads to inhibition of methanol oxidation but reactivation of the surface, as the oxide, which is stable cathodically, leads to another large anodic peak as the former. Therefore, the response during the second and subsequent cycles is exactly the same except for slightly enhanced currents particularly around $+0.46$ V. From the followed several scans, it can be seen that the activity of the Pd-based catalysts remained stable. These data indicate that the rate of
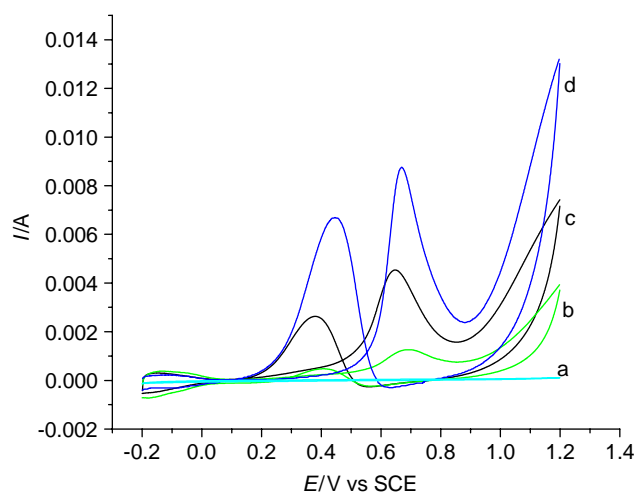

Fig. 5. Cyclic voltammograms in 1 M CH$_3$OH + 1 M H$_2$SO$_4$ for a Pd-catalyzed (reduction of PdCl$_2$ by glycol ethanol) TiO$_2$ nanotube dispersed with Nafion solution on Ti: (a) pure TiO$_2$ nanotubes; (b) pure Pd; (c) 3 wt% Pd–TiO$_2$ nanoparticles; (d) 3 wt% Pd–TiO$_2$ nanotubes. Scan rate 50 mV/s.

methanol adsorption has a small role in determining the response at the Pd-catalyzed TiO$_2$ nanotube surface. Changing the Nafion content of catalyst in DMFCs is known to affect the methanol oxidation activity [15]. However, in a fuel cell, Nafion exhibits an inhibiting role; therefore, it is not possible to remove the Nafion, as it is required for both proton conductivity and stabilization of the catalysts.

Three nanomaterials, TiO$_2$ nanoparticles, nanotubes, and pure Pd samples as substrates having the same content of palladium, were investigated to determine their activities in methanol oxidation, shown in Fig. 5. The pure TiO$_2$ nanotubes/Ti electrode hardly shows any activity for the methanol oxidation. The pure palladium sample was run once to confirm that the activity was much lower than any other two samples. It is clear that the titania nanotube catalyst is the most active, followed

by the nanoparticles and then the pure Pd. The palladium well dispersed on titania tubes with Nafion membrane is the best catalyst because TiO_2 nanotubes have a small size in diameter and therefore higher specific surface area inside and outside, which is preferable for the electrocatalyst. The Nafion-dispersed titania nanotube catalyst performed better than the other two at large current densities. It shows that when using Pd as a methanol oxidation catalyst, titania tubes or other promoting material must be present, otherwise CO poisoning for Pd would greatly lower all activity in methanol oxidation.

3.4. Comparison of different contents of Pd dispersed on TiO_2 nanotubes

Different mass contents of Pd–TiO_2 tube nanomaterials on Ti electrode in $1\,M\ CH_3OH + 1\,M\ H_2SO_4$ have also been considered in Table 1. Definitely, 3 wt% Pd–TiO_2 nanotube catalysts show the most successful current densities on methanol eletrocatalysis and 25 wt% Pd catalysts have the lowest activity overall. It may be that the more the content of palladium dispersed on titania tubes, the more the particle size on the surface. Furthermore, the particle aggregate was harder, which made the surface area become lower. The content of palladium was too little, so that the properties of titania were definite enough and it blocked the activity point of Pd nanoparticles exposure on the surface of the electrode. It would not be efficient in methanol oxidation. As expected, the mass content of Pd on titania nanotubes had the best ratio, about 3 wt% (terified by EDS), which could show the excellent activity for methanol electrooxidation.

4. Conclusions

Eletrocatalytic activity of Pd–titania nanotube composites dispersed with Nafion on titanium electrode was investigated with respect to the oxidation of methanol in H_2SO_4 solution. The Pd–TiO_2 nanotube composite catalysts displayed catalytic activity superior to that of pure Pd and the other TiO_2 substrates. Overall, the relative activities were Pd-nanotubes > Pd-particles > pure Pd. The best mass ratio of Pd that showed great activity for methanol oxidation is 3 wt%. The surface information and the relative oxidation states were confirmed by electrochemistry, TEM and XRD analysis. Of all the catalysts tested, Nafion supported 3 wt% Pd-titania nanotubes give the best methanol

Table 1
Comparison of methanol oxidation activity of different mass ratios of Pd–TiO_2 nanotubes Nafion-dispersed catalysts (at $+0.70\,V$ around)

wt% Pd–TiO_2 nanotubes	Methanol oxidation peak current/10^{-3}A (at $+0.70\,V$ around)
0	0.0
1.0	1.2
3.0	9.0
5.0	6.3
8.0	5.2
25.0	1.1
100	1.1

All the contents of palladium were tested by EDS.

oxidation activity due to the optimum combination of catalytic activity and TiO_2 morphologies accessibility.

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