

Short communication

Pd electrocatalyst supported on carbonized TiO₂ nanotube for ethanol oxidation

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Received 5 July 2006; received in revised form 18 September 2006; accepted 19 September 2006
Available online 27 October 2006

Abstract

Pd electrocatalysts supported on carbonized TiO₂ nanotube (Pd/TiO₂C) have been prepared and used for the oxidation of ethanol in alkaline media. The conducting treatment of TiO₂ nanotube is performed by the carbonization using the organic polymer. The as-prepared Pd/TiO₂C electrocatalyst shows a higher surface area from the morphology observation and electrochemical measurement compared to Pd/C electrocatalyst at the same loadings of Pd. It is found that the Pd/TiO₂C electrocatalyst with the 1:1 mass ratio of Pd to TiO₂C gives best performance for ethanol oxidation in alkaline media. The results prove that the Pd/TiO₂C electrocatalyst is not only superior in activity for ethanol oxidation but also more stable during the constant current density polarization in alkaline media in comparison with Pd/C electrocatalyst.

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Keywords: Titania; Carbonization; Alcohol oxidation; Alkaline media

1. Introduction

Noble metal catalysts supported on ceria [1–3], magnesia [4,5], zirconia [6], nickel protoxide [7,8], alumina [9,10], iron oxide [11], titania [12,13] and the other oxides [14,15] show promising performance for the oxidation of alcohols and CO. These oxide supports are able to stabilize and disperse adequately a number of active phases, as well as to retain a high surface area.

Recently, titania (TiO₂) nanomaterial has been paid significant attention due to its features related to the semiconductive nature and its ability to serve as a host for hydrogen insertion, which makes it a valuable functional material in many areas of such as solar light conversion [16], self-cleaning properties [17], hydrogen insertion [18] or the dielectric capacitors [19], etc. The nanotubule structure of TiO₂ seems to increase the dispersion of active materials and consequently results in the enhancement of capacitance. Moreover, nanoscaled TiO₂ is also widely used as the support of catalysts for the catalytic combustion of methane or sewage disposal [20,21]. These properties are def-

initely dependent on its physical and chemical characteristics such as crystal structure, morphology and surface structure. The large BET surface area, high stability and homogenous size distribution are helpful to increase the gas/liquid interfacial area. Therefore, as a support it can improve the catalytic activity for a certain reaction by increasing the surface area [22,23]. However, TiO₂ nanotube is not suitable for using as the support alone for the electrocatalysts because of its poor conductivity. In this paper, this problem can be conquered through the carbonization of TiO₂ by using the organic polymer.

It has been evidenced that the metal doped oxides are a new class of oxidation catalysts [24,25]. Chrétien and co-workers used density functional theory to examine different metal doped TiO₂ (1 1 0) for CO oxidation and found that Pd-doped TiO₂ (1 1 0) has lower desorption energy of the bounded oxygen than that of Pt or Au-doped TiO₂ (1 1 0) [26]. Pd-based electrocatalyst is a very active catalyst for the total oxidation of alcohols or hydrocarbons according to the experimental results, especially in alkaline solution [27]. Our previous work showed that the addition of oxides could greatly improve the performance of Pd/C for alcohol oxidation [28].

TiO₂ nanotubes were adopted as chemical catalyst support for water treatment and methane reforming as previously reported [20,21]. Unlike the chemical catalyst, however, high conduc-

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tivity is necessary for electrocatalyst. To our best knowledge, carbonization was never been used to enhance the conductivity of TiO₂ nanotubes. In this paper, we report the use of carbonized TiO₂ nanotube prepared by the carbonization using the organic polymer as the support of Pd electrocatalyst (denoted as Pd/TiO₂C) for the oxidation of ethanol in alkaline media.

2. Experimental

The method employed for the synthesis of titania nanotubes from titania nanoparticles (A.R., Beijing Chemical Factory, China) was a mild hydrothermal method as reported in literatures [29,30]. TiO₂ nanotubes were covered a carbon layer on the surface through the following procedure prior to loading the electrocatalyst. A mixture of 50.0 mg TiO₂ nanotube and 94.7 mg poly (ethylene glycol) 600 (A.R., Guangdong Xilong Chemical Factory, China) was placed in a quartz tube and Ar flowed through the quartz tube at 500 sccm for 60 min before heating. The flow rate of Ar was decreased to 100 sccm and maintained for 30 min at the temperature of 600 °C. The product with the weight ratio of TiO₂:C = 1:1 was obtained under such conditions. Pd/TiO₂C electrocatalyst was prepared by the reduction of PdCl₂ (4.7 ml, 0.1 mol dm⁻³) (A.R., Guangdong Xilong Chemical Factory) in aqueous solution on TiO₂C (50.0 mg) powders. The ratio of Pd to TiO₂C was controlled by the stoichiometric calculation and confirmed by EDX measurement. The electrode preparation procedure is as follows: 4.5 mg Pd/C (prepared using the same method as reported in Ref. [15]) or Pd/TiO₂C powders were firstly dispersed in 5.0 ml isopropyl aqueous solution ($V_{\text{alcohol}}:V_{\text{water}} = 1:3$) with 1.0 ml of 0.5 wt.% Nafion suspension under ultrasonic stirring. The well-mixed electrocatalyst ink (0.2 ml) was deposited onto the surface of a graphite rod with the geometric area of 0.5 cm² and dried at 80 °C for 30 min. The Pd loadings on the Pd/C and Pd/TiO₂C electrodes were controlled at 0.3 mg cm⁻².

The experiments were carried out at 30 °C controlled by a water-bath thermostat. Structural and morphological characterization was carried out on a JOEP JEM-2010 (JEOL Ltd.) transmission electron microscopy (TEM) operating at 200 kV, a scanning electron microscope (SEM) (LEO 1530 VP, Germany) and an X-ray diffractometer D/Max-III A (Rigaku Co., Japan, Cu K α 1 ($\lambda = 1.54056 \text{ \AA}$) radiation source). All electrochemical measurements were conducted in a three-electrode cell on an IM6e electrochemical workstation (Zahner-Electrik, Germany). A platinum foil (3.0 cm²) and Hg/HgO (1.0 mol dm⁻³ KOH) were used as counter and reference electrodes, respectively.

3. Results and discussion

A typical TEM image of TiO₂ nanotubes is shown in Fig. 1(a). The hollow nature of the nanotubes can be clearly observed from the inset in Fig. 1(a). The inner diameter, outer diameter and length of the TiO₂ nanotubes range from 15 to 20 nm, 20 to 30 nm and 1 to 5 μm , respectively. It is known that the performance of an electrode depends on the factors of porous mass, agglomerate size, internal porosity, real surface area and binder content [22]. It is obvious that the proper open meso-

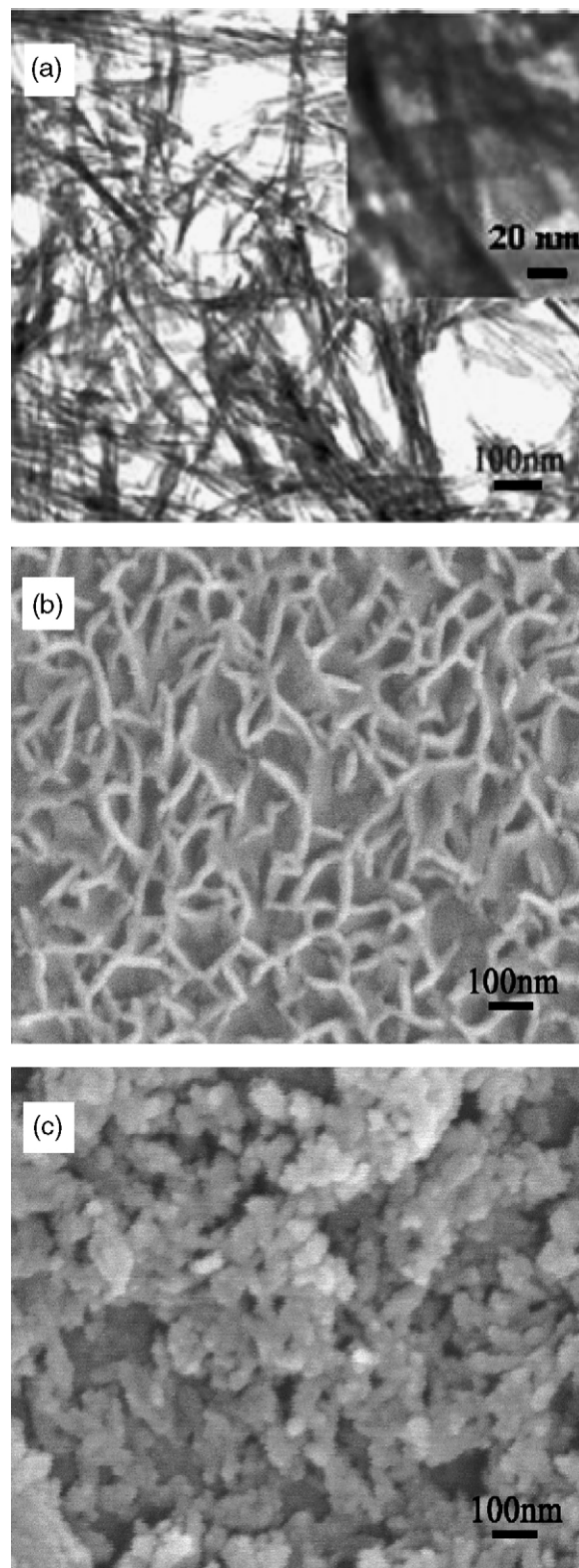


Fig. 1. (a) TEM image of TiO₂ nanotube and SEM micrographs of (b) TiO₂C and (c) Pd/TiO₂C. The inset in (a) is the enlarged TEM image.

porous network of nanotube allows quick charge transportation in the material and this is helpful for the electrolyte ions to access the active materials. As seen from the SEM micrographs in Fig. 1(b and c), TiO₂C and Pd/TiO₂C present a porous struc-

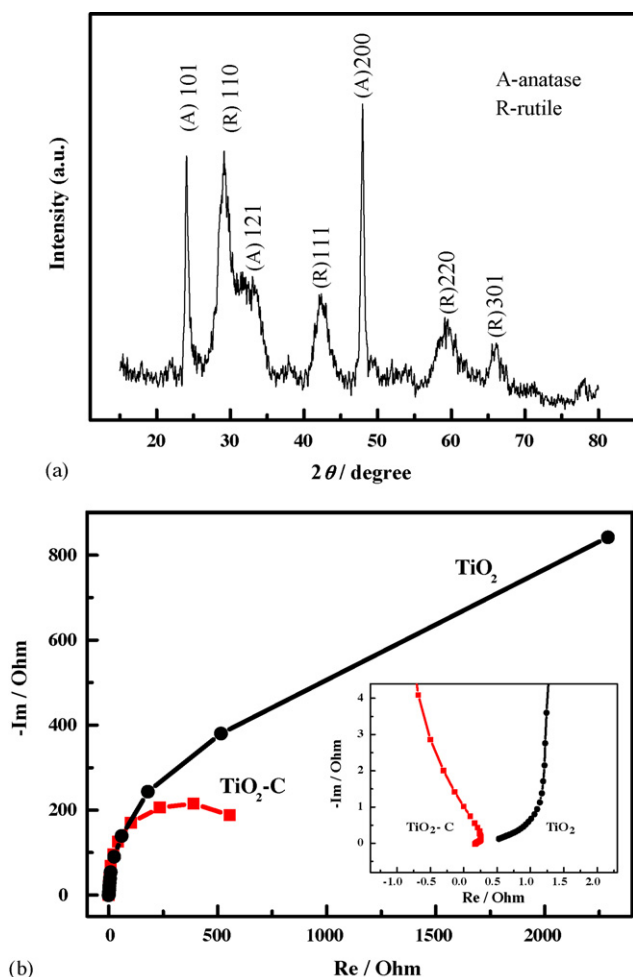


Fig. 2. (a) X-ray diffraction pattern of TiO_2 nanotubes. (b) AC-impedance spectra of TiO_2 and $\text{TiO}_2\text{-C}$ electrodes in $1.0 \text{ mol dm}^{-3} \text{ KOH}/1.0 \text{ mol dm}^{-3}$ ethanol aqueous solution. Inset is the partial amplification AC-impedance spectra.

ture, which will provide them with higher surface area and thus enhance their catalytic activity. Fig. 2(a) shows the XRD pattern of the TiO_2 nanotubes. It can be clearly seen from Fig. 2(a) that TiO_2 nanotubes are crystals with the co-existence of anatase and rutile.

AC-impedance technique was used to measure the resistances of the TiO_2 nanotube before and after carbonization. It is known that the resistance of the system was determined by the high frequency intercept of the AC-impedance response on the real axis of the Nyquist plot. Fig. 2(b) shows the AC-impedance spectra of TiO_2 and $\text{TiO}_2\text{-C}$ electrodes in $1.0 \text{ mol dm}^{-3} \text{ KOH}/1.0 \text{ mol dm}^{-3}$ ethanol aqueous solution at an open-circuit voltage (OCV). It shows that the arch for $\text{TiO}_2\text{-C}$ is much smaller than that of pure TiO_2 , indicating that the value of resistance of the carbonized TiO_2 nanotube is significantly lower than that of the pure $\text{TiO}_2\text{-C}$. This suggests that after the carbonization, the conductivity of the TiO_2 nanotubes was significantly increased. It is very helpful to decrease the ohmic polarization during the electrode process.

As previously reported, the activity of ethanol oxidation on Pt- CeO_2/C or Pd- NiO/C electrocatalysts was better than that of Pt/C or Pd/C electrocatalysts. Here, the conducting TiO_2 nanotube supported Pd electrocatalyst gave even better performance

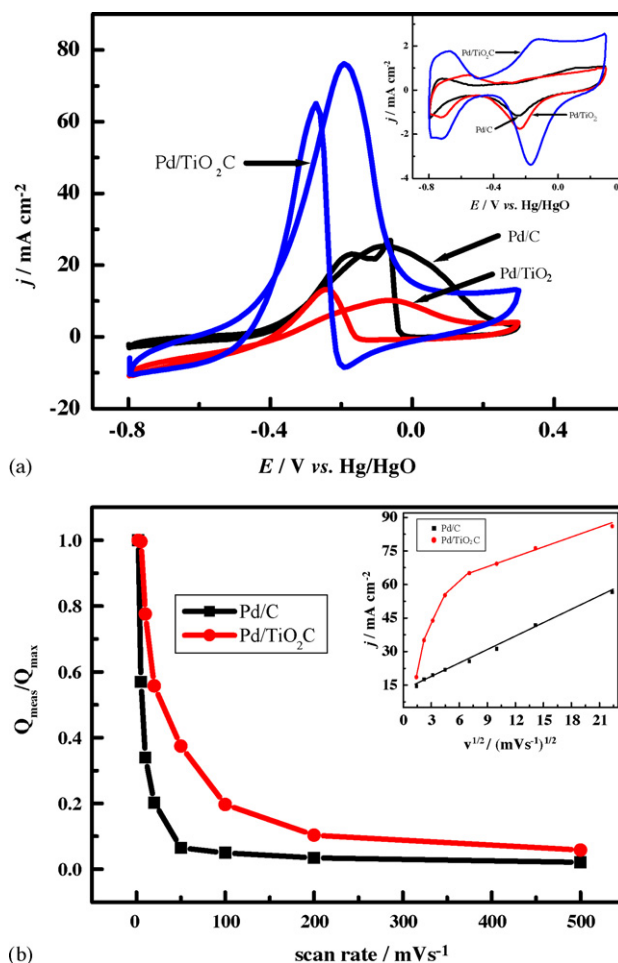


Fig. 3. (a) Cyclic voltammograms of ethanol oxidation on Pd/C, Pd/ TiO_2 and Pd/ $\text{TiO}_2\text{-C}$ in $1.0 \text{ mol dm}^{-3} \text{ KOH}/1.0 \text{ mol dm}^{-3}$ ethanol solution, 303 K, scan rate: 50 mVs^{-1} . Inset is the CVs in ethanol-free $1.0 \text{ mol dm}^{-3} \text{ KOH}$ solution to be used to compare the surface area. (b) Plot of normalized charge of anodic peak and scan rate on Pd/C electrode and Pd/ $\text{TiO}_2\text{-C}$ electrode. Inset is the plots of the peak current density against the square root of scan rate for both electrodes.

as shown in Fig. 3(a). The onset potential of the ethanol oxidation on Pd/ $\text{TiO}_2\text{-C}$ electrocatalyst shows a significant negative shift of about 150 mV and a three-fold peak current densities compared to the corresponding values over Pd/C. The results indicate that the better performance of ethanol oxidation on Pd/ $\text{TiO}_2\text{-C}$ electrocatalyst can be attributed to the increase in the surface area because of the porous structure of TiO_2 nanotube as shown in Fig. 1(a) [12].

The relationship between ethanol oxidation charge and scan rate on Pd/C electrode and Pd/ $\text{TiO}_2\text{-C}$ electrode was examined and the results are shown in Fig. 3(b). Q_x represents the integrated charge of anodic peak for ethanol oxidation at different scan rates. Q_{max} denotes for the charge at the scan rate of 2 mVs^{-1} . It can be seen from Fig. 3(b) that the charge decreases with the increase in the scan rate. This decrease on Pd/C electrode was much sharper than that on Pd/ $\text{TiO}_2\text{-C}$ electrode, indicating that the mass transport on Pd/C electrode was strictly limited. By plotting the anodic peak current density against the square root of the scan rate, a linear relationship can be found on Pd/C electrode (inset in Fig. 3(b)). However,

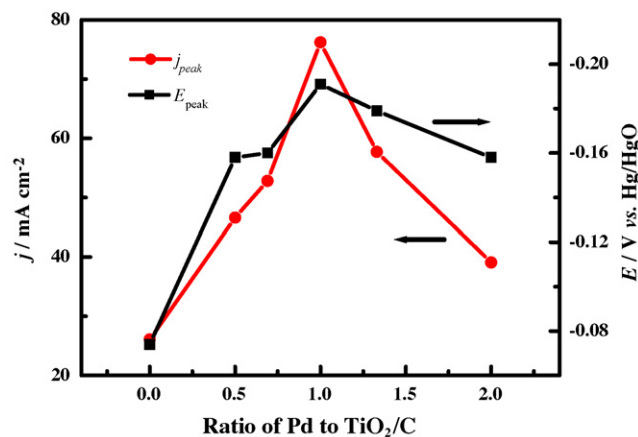


Fig. 4. Comparison of the peak current densities and onset potentials at different ratios of Pd to TiO₂C for ethanol oxidation in 1.0 mol dm⁻³ KOH/1.0 mol dm⁻³ ethanol solution. 0.3 mg cm⁻² Pd, 303 K and 0.05 V s⁻¹.

the linear relationship only appeared at higher scan rates in the case of Pd/TiO₂C electrode. The peak current density was proportional to the scan rate instead of the square root of scan rate at lower scan rates. The results reveal that the oxidation of ethanol on Pd/C electrode is controlled by the concentration polarization. While, the oxidation of ethanol on Pd/TiO₂C electrode is controlled by activation polarization at lower scan rates due to the porous structure of TiO₂ nanotubes, which allows ethanol to access the active sites easier.

The mass ratio of Pd to TiO₂C was optimized to obtain the best performance for ethanol oxidation. The activity of the electrocatalyst was evaluated by comparing the anodic peak current density and the onset potential of ethanol oxidation on a cyclic voltammogram. Pd/TiO₂C electrocatalysts with different mass ratios of Pd to TiO₂C at the fixed Pd loading of 0.30 mg cm⁻² were examined by cyclic voltammetry. Fig. 4 compares the anodic current densities and onset potentials of ethanol oxidation over Pd/TiO₂C at different ratios of Pd to TiO₂C. It can be clearly seen from Fig. 4 that Pd/TiO₂C electrocatalyst with the 1:1 mass ratio of Pd to TiO₂C gave the best performance for ethanol oxidation in alkaline media in term of the peak current density and the onset potential. It is understandable that the catalytic activity increases with the increase in the percentage of Pd in the Pd/TiO₂C when the ratio of Pd to TiO₂C is less than 1 since Pd is the main component for the catalytic reaction. The decrease in the catalytic activity at higher Pd percentages is probably due to the decrease in the surface area since the higher Pd loadings would flat the porous structure. Therefore,

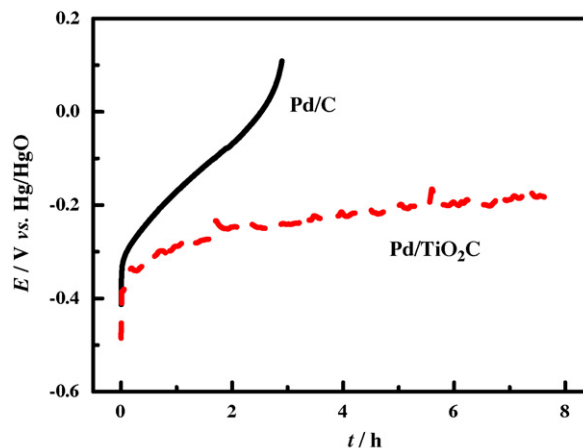


Fig. 5. Chronopotentiometric curves of ethanol oxidation on Pd/C and Pd/TiO₂C electrodes at 3.0 mA cm⁻² in 1.0 mol dm⁻³ KOH/1.0 mol dm⁻³ ethanol solution.

Pd/TiO₂C electrocatalyst with the ratio of Pd to TiO₂C of 1:1 was adopted for the further investigations.

In order to check the stability of Pd/TiO₂C, the steady-state measurement was conducted to evaluate the as-prepared Pd/TiO₂C electrocatalyst for ethanol oxidation. Fig. 5 shows the respective chronopotentiometric curves for ethanol oxidation on Pd/C and Pd/TiO₂C electrodes at 3 mA cm⁻². The oxidation of ethanol on Pd/TiO₂C electrode was relatively stable at low potentials. However, on the Pd/C electrode, the potential was higher at the same current density and the potential finally shifted to a higher value for oxygen evolution instead of the oxidation of ethanol due to the concentration polarization. So far, we have not got the information whether the Pd-based electrocatalysts can cleave the C–C bond in ethanol molecule to form CO-like poisoning species in alkaline media. In situ FTIR study is in progress to find the mechanism of the ethanol oxidation on the Pd/TiO₂C electrocatalyst.

The oxidation of methanol, glycerol and ethylene glycol (EG) on Pd/TiO₂C electrocatalyst was also examined besides ethanol. Table 1 summarizes the corresponding values of the onset potentials (E_s), peak potentials (E_p) and peak current densities (j_p) for alcohols oxidation on Pd/C and Pd/TiO₂C electrodes, respectively. In all the cases, Pd/TiO₂C electrocatalyst shows the better performance for alcohol oxidation than that of Pd/C. It is well known that the oxidation of ethanol is more sluggish than that of methanol on Pt-based electrocatalysts in acidic media [31–33]. However, from Table 1 one can distinguish that Pd/TiO₂C exhibits superior activity for ethanol oxidation in comparison

Table 1
Summary of the onset potentials (E_s), peak potentials (E_p) and peak current densities (j_p) of alcohols oxidation on Pd/C and Pd/TiO₂C electrodes in 1.0 mol dm⁻³ KOH/1.0 mol dm⁻³ alcohol aqueous solutions at 303 K

Alcohols	Pd/C			Pd/TiO ₂ C		
	E_s (V)	E_p (V)	j_p (mA cm ⁻²)	E_s (V)	E_p (V)	j_p (mA cm ⁻²)
Methanol	-0.45	-0.131	22.8	-0.50	-0.155	39.8
Ethanol	-0.49	-0.074	25.4	-0.62	-0.191	76.2
Glycerol	-0.38	-0.035	27.7	-0.47	-0.050	75.9
EG	-0.46	-0.066	29.4	-0.52	-0.121	88.1

with methanol in alkaline media. From the experimental results, we suggest that Pd/TiO₂C is a promising electrocatalyst for the direct alkaline ethanol fuel cell. Ethanol is a renewable liquid fuel and can be easily produced in large quantity by fermentation of sugar-containing raw materials [34,35]. Direct ethanol fuel cells present distinct potential advantages over combustion engines and hydrogen fuel cells for portable and remote power applications.

4. Conclusion

The conductivity of TiO₂ nanotube was improved by the carbonization using organic polymer. It was revealed that the carbonized TiO₂ nanotube could significantly improve performance of the Pd-based electrocatalysts for ethanol oxidation in alkaline media. They are markedly superior to those of pure Pd electrocatalysts. The possible reason is that the open mesoporous network of TiO₂ nanotube can make the Pd/TiO₂C electrocatalyst porous and loose structure to increase the surface active sites and consequently the activity for ethanol oxidation is enhanced. The fact that the Pd/TiO₂C electrocatalyst is stable during the constant current density polarization in alkaline media means that the cleavage of the C–C bond of the ethanol is difficult on Pd/TiO₂C electrocatalyst to form strongly adsorbed poisoning species.

Acknowledgments

The authors gratefully acknowledge the support by the NNSFC (20476108), the NSF of Guangdong Province (04105500), the Guangzhou Science and Technology Key Project (200523-D0251) and the Guangdong Science and Technology Key Projects (2005A11001002, 2005A11004001).

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