



Short communication

Building three-dimensional Pt catalysts on TiO₂ nanorod arrays for effective ethanol electrooxidation

Xiaoshan He, Chenguo Hu*

Department of Applied Physics, Chongqing University, 174 Shapingba Street, Chongqing 400044, PR China

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ABSTRACT

Pt nanoparticles on TiO₂ nanorod arrays have been prepared and used for the electrooxidation of ethanol in acidic and alkaline media. The vertically aligned TiO₂ nanorod arrays provide a three-dimensional frame for supporting Pt nanoparticles. FESEM and TEM show that the Pt nanoparticles about 3 nm in diameter are evenly distributed on the surface of TiO₂ nanorods. Cyclic voltammetry and chronoamperometry are performed to investigate electrochemical properties of Pt/TiO₂/Ti, Pt/C, and Pt/Ti electrocatalysts. The Pt/TiO₂/Ti electrocatalyst shows better catalytic activity and higher catalytic stability compared with other electrocatalysts.

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1. Introduction

The direct alcohol fuel cells (DAFCs) have attracted more and more attentions due to their potential applications in transportation and portable electronic devices [1–3]. In these alcohols, ethanol is a promising candidate for direct conversion into electrical energy in the direct alcohol fuel cell systems, mainly because ethanol is much less toxic and inexpensive, and has less crossover effect than methanol [4,5]. Moreover, ethanol is a green fuel and can be easily produced in large quantities from agricultural products or biomass [6–8]. However, the low catalytic activity and slow reaction kinetics of ethanol electrooxidation is a main obstacle for the application of direct ethanol fuel cells (DEFCs) currently [9–11].

Recently, some groups have reported that an addition of oxide is efficient to improve catalytic activity of Pt and its CO tolerance for alcohol electrooxidation [12–16]. TiO₂, as one of the semiconductive oxide, has been widely studied for its special photoelectric properties. In addition, TiO₂ is stable in both acidic and alkaline solutions, which has shown high activity of catalyst for the reduction of some small organic molecules [17,18]. Many recent studies have reported that TiO₂ electrode as the support of Pt has highly catalytic activity and CO tolerance for alcohol electrooxidation owing to synergistic effect between Pt nanoparticles and the TiO₂ support [19,20]. Therefore, a three-dimensional support built by TiO₂ nanorod arrays could not only provide high surface area for Pt loading but also improve catalytic activities of electrocatalyst.

In this paper, vertically aligned TiO₂ nanorod arrays are employed as a three-dimensional support for Pt nanoparticles. The TiO₂ nanorod arrays are prepared directly on the Ti foil via a facile hydrothermal method, which is environmentally friendly and template-free. Pt nanoparticles about 3 nm in diameter are uniformly deposited on the vertically aligned TiO₂ nanorod arrays, constructing a novel three-dimensional catalyst for effective electrocatalytic oxidation of ethanol. The TiO₂ nanorod arrays on Ti foil (TiO₂/Ti), Pt catalysts deposited on TiO₂/Ti (Pt/TiO₂/Ti) and Ti foil (Pt/Ti) are characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDS). In addition, the performances of the electrocatalysts for the ethanol electrooxidation are studied via cyclic voltammetry (CV) and chronoamperometry in both acidic and alkaline media. The Pt/TiO₂/Ti electrocatalyst shows a higher electrochemically active surface area from the three dimensional morphology and much better performances in electrochemical measurements compared with other electrocatalysts, although they have the same loading of Pt. It has been proved that the Pt/TiO₂/Ti electrocatalyst could be the desired catalyst with advantage of superior activity in the DEFCs.

2. Experimental

2.1. Chemicals

Titanium foil (99.94%), 0.5 mm thick and silver paste were purchased from Sigma–Aldrich and SPI Supplies, respectively. H₂PtCl₆, ethanol, acetone, H₂SO₄, KOH and HCl (36%) were from Chongqing Chemical Reagent Company. Carbon black (Vulcan XC72R) was

* Corresponding author. Tel.: +86 23 65104741; fax: +86 23 65111245.

E-mail addresses: hucg@cqu.edu.cn, hu.chenguo@yahoo.com (C. Hu).

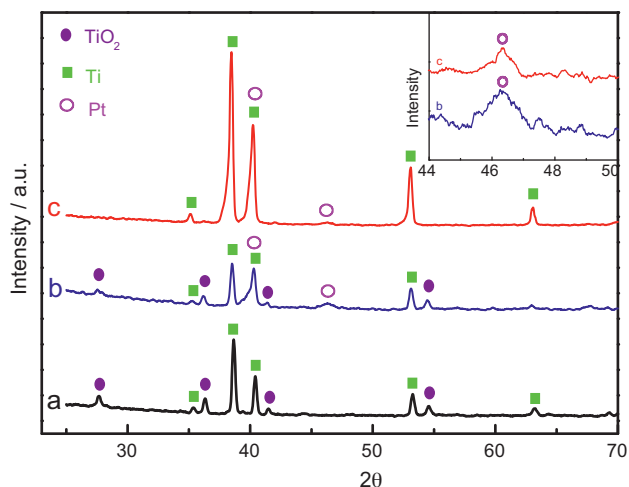


Fig. 1. XRD patterns of the samples: TiO₂/Ti (a), Pt/TiO₂/Ti (b), Pt/Ti (c).

from CABOT Corp. All chemicals were of analytical grade and were used as received. Deionized water was used to prepare all the solutions.

2.2. Preparation of Pt/TiO₂/Ti electrocatalyst

The preparation of the vertically aligned TiO₂ nanorod arrays growing directly on Ti foils has been reported previously [21]. Typically, Ti foil was first ultrasonically washed in an acetone–ethanol (1:1 in volume) mixture for 10 min, and then chemically etched in 18% HCl aqueous solution at approximately 80 °C for about 10 min. Then the pre-etched Ti foil was placed in 5 mL aqueous solution containing 0.2 mL HCl solution (36%) and heated at 200 °C for 10 h. To fabricate the Pt nanoparticles on TiO₂ nanorod arrays, the prepared TiO₂/Ti foil was calcined at 380 °C for 15 min after dropping 1.0 mM H₂PtCl₆ solution on it. Finally, the sample was washed with deionized water and dried in air.

The Pt/TiO₂/Ti electrocatalyst was fabricated by contacting a copper wire using silver paste. Then, it was covered with epoxy resin, leaving 5 mm × 4 mm area open. Pt loading on the electrocatalyst was 0.01 mg cm⁻². Pt/Ti electrocatalyst was prepared in the same process. To compare catalysis of the Pt/TiO₂/Ti electrocatalyst with other common Pt-based catalyst, Pt supported on carbon black

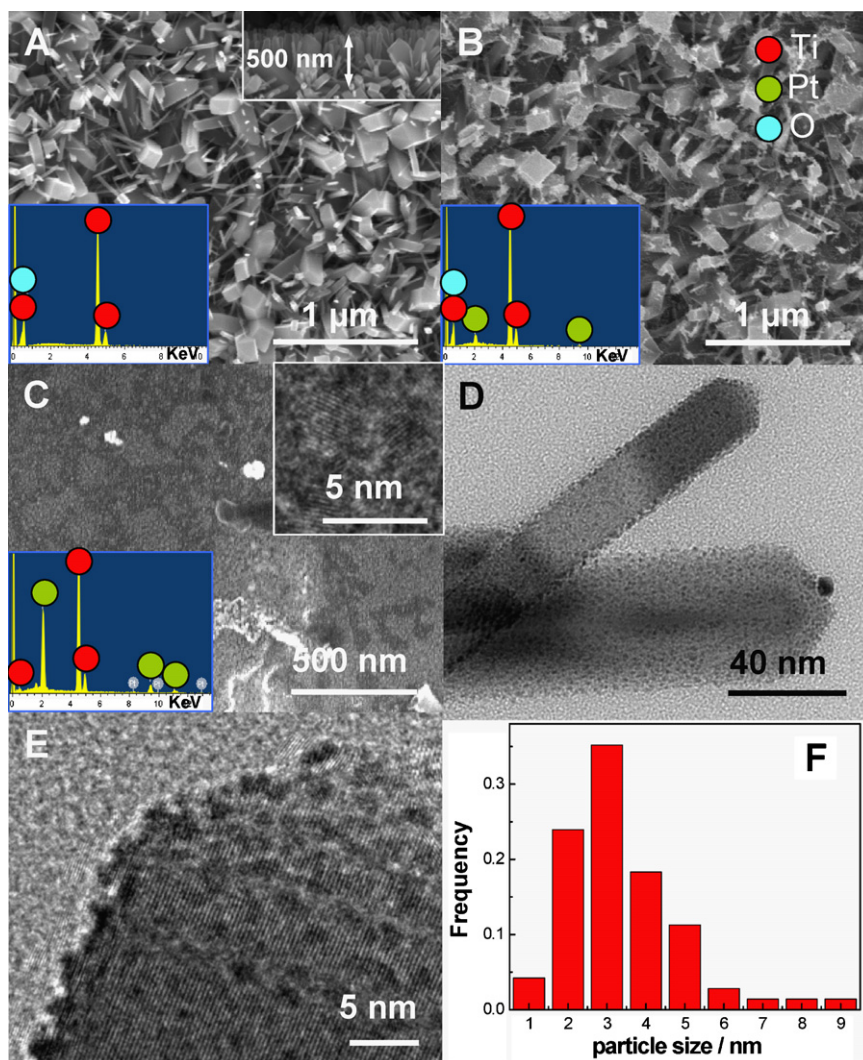


Fig. 2. FESEM images of TiO₂/Ti (A), Pt/TiO₂/Ti (B), Pt/Ti (C). TEM (D) and HRTEM (E) images of Pt/TiO₂/Ti. F is the histogram of Pt nanoparticle size distribution. The insets of (A–C) are the corresponding EDS results.

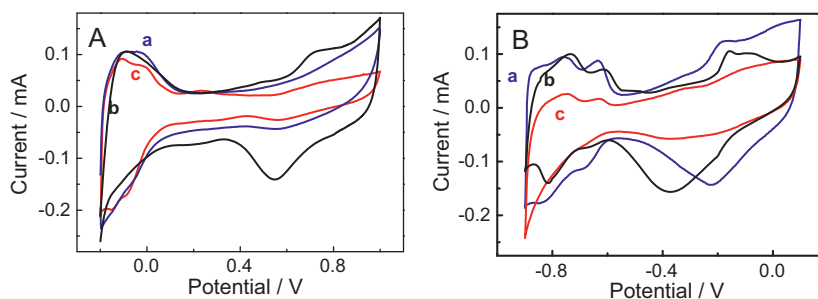


Fig. 3. CVs of the Pt/TiO₂/Ti (a), Pt/C (b), and Pt/Ti (c) electrocatalysts in 0.5 M H₂SO₄ (A) and 1.0 M KOH (B) with a sweep rate of 50 mV s⁻¹.

(Pt/C) was prepared as the reported [22] with the same loading of 0.01 mg cm⁻² Pt.

2.3. Instruments and measurements

The structures of the samples were characterized by XRD (XRD-6000, Shimadzu Co., Japan) using Cu K α as the radiation source. The size and morphology of the prepared products were measured by FESEM (FEI Nova 400, at 20 kV) and high resolution transmission electron microscopy (HRTEM, ZEISS LIBRA 200 FETEM, at 20 kV). The composition of the samples was analyzed by EDS (TESCAN VEGAII, at 20 kV). LK98B(II) electrochemical workstation (Tianjing Lanlike Instruments) was employed for the electrochemical measurements, which were carried out with the conventional three-electrode electrochemical cell. Pt foil and Ag/AgCl (saturated KCl) was used respectively as the counter electrode and reference electrode. CVs were conducted at a rate of 50 mV s⁻¹ in acidic or alkaline solution. The chronoamperometric curves were recorded in 0.5 M H₂SO₄ containing 1.0 M C₂H₅OH at 0.7 V and 1.0 M KOH containing 1.0 M C₂H₅OH at -0.2 V for 600 s. All the experiments were performed at room temperature (20 °C).

3. Results and discussion

3.1. Characterization of the electrocatalysts

The structures of TiO₂/Ti (a), Pt/TiO₂/Ti (b) and Pt/Ti (c) are shown in Fig. 1. Crystalline features are evident in all XRD profiles. The peaks at the 2 θ of 35.16, 38.46, 40.22, 53.1 and 63.04 correspond to the (1 0 0), (0 0 2), (1 0 1), (1 0 2) and (1 1 0) of Ti (JCPDS 44-1294). The 2 θ of 27.64, 36.38, 41.54 and 54.56 correspond to the (1 1 0), (1 0 1), (1 1 1) and (2 1 1) of rutile TiO₂ (JCPDS 89-4920). The peak around the 40° for Pt is overlapped with the peak of Ti. However, the specific peak at 46.51° for Pt can be distinguished after being magnified in the inset of Fig. 1, though the intensity is relatively weak.

The surface morphologies of samples are shown in Fig. 2. Fig. 2A presents a typical FESEM of the vertically aligned TiO₂ nanorod arrays growing directly on a Ti foil. The Ti foil is fully covered by highly dense and uniform TiO₂ nanorods with a size of 50–100 nm in width, 400–500 nm in length. After being deposited by Pt, the TiO₂/Ti substrate is covered by Pt nanoparticles. From the Fig. 2B, numerous Pt nanoparticles are loaded on the TiO₂ nanorods. Fig. 2C

is the morphology of the Pt/Ti electrocatalyst. The Pt nanoparticles are distributed on the surface of the Ti foil. Inset is the HRTEM image of Pt nanoparticles, showing the Pt nanoparticles are about 3 nm in diameter. The compositions of the TiO₂/Ti substrate, Pt/TiO₂/Ti and Pt/Ti electrocatalysts are analyzed by EDS, as shown in the inset of Fig. 2A, B, and C, respectively. The results are consistent with those of XRD. For further examination of the details of Pt/TiO₂ nanorods, they are characterized by HRTEM, as shown in Fig. 2D and E. It can be seen that the Pt nanoparticles about 3 nm in diameter are well supported on the TiO₂ nanorods, in good agreement with the FESEM results. Fig. 2F shows the corresponding histograms of size distribution for the Pt nanoparticles.

3.2. Electrooxidation of ethanol on the Pt/TiO₂/Ti, Pt/C and Pt/Ti electrocatalysts

Fig. 3 presents the CV curves of the Pt/TiO₂/Ti, Pt/C and Pt/Ti electrocatalysts recorded in 0.5 M H₂SO₄ (A) and 1.0 M KOH (B) solutions. In the acidic media, there are two peaks at -0.11 and -0.02 V for the Pt/TiO₂/Ti electrocatalysts due to the hydrogen adsorption/desorption. And in the alkaline media, there exist similar peaks at -0.76 and -0.63 V. For comparison, Pt/C and Pt/Ti electrocatalysts are also studied. However, all the peaks of Pt/TiO₂/Ti electrocatalyst are stronger than that of other electrocatalysts. The electrochemically active surface area (*A*) can then be found using the area of hydrogen adsorption/desorption peaks [23], as shown in Table 1. Due to the three-dimensional structure of the TiO₂ support for Pt nanoparticles, the Pt/TiO₂/Ti electrocatalyst has a larger *A* compared with the Pt/C and Pt/Ti electrocatalysts.

The performances of the Pt/TiO₂/Ti, Pt/C and Pt/Ti electrocatalysts for ethanol electrooxidation in acidic (A) and alkaline (B) media are comparatively shown in Fig. 4. These electrocatalysts are active for ethanol oxidation. To make comparison more facile, current densities are calculated by the electrochemical determined surface area. And the comparisons of the electrochemical performances on electrocatalysts are shown in Table 2. In the acidic media, the CV curve shows two oxidation peaks for these electrocatalysts. The forward scan peak currents present the electrochemical oxidation reaction of the freshly chemisorbed species coming from ethanol solution. The backward scan peak is primarily related with removal of carbonaceous species which are not completely oxidized in the forward scan [24]. The slightly more negative onset potential of the Pt/TiO₂/Ti demonstrates that the

Table 1

The electrochemical active surface area (*A*) of Pt/TiO₂/Ti, Pt/C, and Pt/Ti electrocatalyst with geometric area: 0.20 cm² and the increased surface area relative to the geometric area.

Electrocatalyst	Pt/TiO ₂ /Ti		Pt/C		Pt/Ti	
	Acidic media	Alkaline media	Acidic media	Alkaline media	Acidic media	Alkaline media
<i>A</i> (cm ²)	0.84	1.41	0.81	1.03	0.70	0.58
Enhancement	4.2	7.05	4.05	5.15	3.5	2.9

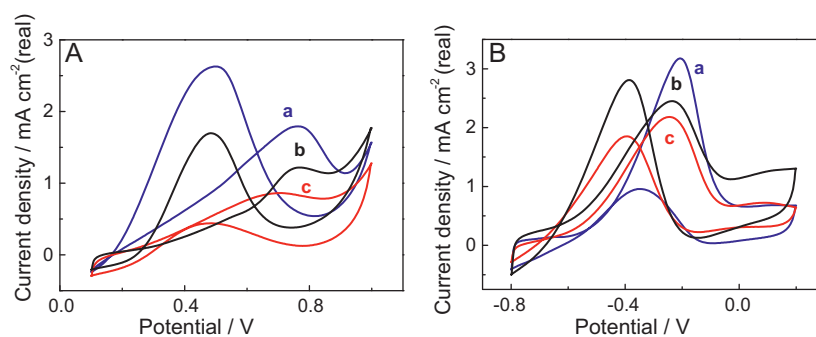


Fig. 4. CVs of the Pt/TiO₂/Ti (a), Pt/C (b), and Pt/Ti (c) electrocatalysts in 0.5 M H₂SO₄ containing 1.0 M C₂H₅OH (A), 1.0 M KOH containing 1.0 M C₂H₅OH (B) with a sweep rate of 50 mV s⁻¹.

Table 2

Comparison of electrochemical performance of ethanol electrooxidation on Pt/TiO₂/Ti, Pt/C, and Pt/Ti electrocatalyst with Pt loading: 0.01 mg cm⁻².

Electrocatalyst	Pt/TiO ₂ /Ti		Pt/C		Pt/Ti	
	Acidic media	Alkaline media	Acidic media	Alkaline media	Acidic media	Alkaline media
Onset potential (V)	0.34	-0.60	0.35	-0.61	0.37	-0.59
Peak potential (V)	0.76	-0.21	0.75	-0.22	0.71	-0.24
Peak current density (mA cm ⁻²)	1.81	3.20	1.22	2.46	0.88	2.19

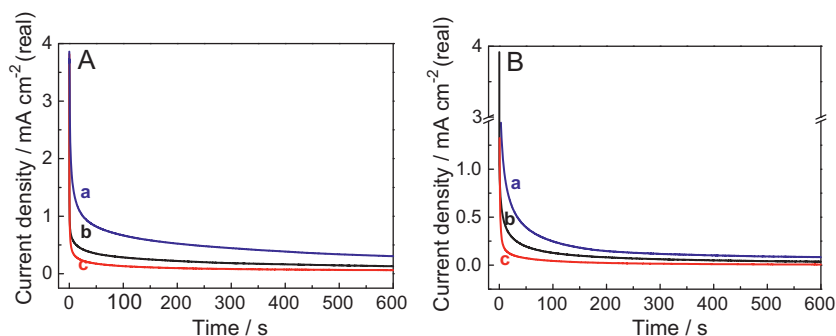


Fig. 5. Chronoamperometric curves of the Pt/TiO₂/Ti (a), Pt/C (b), and Pt/Ti (c) electrocatalysts in 0.5 M H₂SO₄ containing 1.0 M C₂H₅OH (A) at 0.7 V, 1.0 M KOH containing 1.0 M C₂H₅OH (B) at -0.2 V.

ethanol oxidizes more readily on this surface [25]. And the peak current densities are almost twice higher for the reaction on Pt/TiO₂/Ti than that on Pt/Ti. The much better electrocatalytic performance of the Pt/TiO₂/Ti for ethanol electrooxidation can be attributed to the synergistic effect between the nanosized Pt catalyst and the TiO₂ support [19]. In alkaline media, two oxidation peaks are observed for these electrocatalysts. Similarly, the Pt/TiO₂/Ti shows higher catalytic activity compared with Pt/C and Pt/Ti electrocatalysts. This implies that the Pt/TiO₂/Ti electrocatalyst could provide a better catalytic activity for ethanol electrooxidation in both acidic and alkaline media.

The electrocatalytic stability of the Pt/TiO₂/Ti, Pt/C and Pt/Ti electrocatalysts for ethanol electrooxidation in acidic (A) and alkaline (B) media have been investigated by chronoamperometric tests and the corresponding curves as are shown in Fig. 5. All the three electrocatalysts show a current decay in the ethanol electrooxidation reaction with test time. The Pt/TiO₂/Ti shows a moderate current density decay. The current densities decrease first and then reach a constant over the experimental period. At the end of the experimental period, the current density of the Pt/TiO₂/Ti is higher than that of the Pt/C and Pt/Ti electrocatalysts, especially in acidic media. The current decay is resulted from the blocking of the surface with CO_{ad} species. However, it is also caused by the time dependent adsorption of the strongly bound irreversible OH_{ad} species in alkaline media [26]. CO_{ad} species could be effectively oxidized and removed from the Pt nanoparticles on the Pt/TiO₂/Ti

electrocatalyst so that the catalytic oxidation of ethanol proceeds more efficiently. The results imply that the Pt/TiO₂/Ti electrocatalyst exhibits higher stability than other electrocatalysts.

4. Conclusions

The vertically aligned TiO₂ nanorod arrays prepared directly on the Ti foil are employed as supports for Pt nanoparticles to build a three-dimensional catalyst. FESEM and HRTEM observations reveal that the Pt nanoparticles about 3 nm in diameter are uniformly dispersed on the TiO₂ nanorod arrays. Because of the three-dimensional structure of the TiO₂ support for well-dispersed Pt nanoparticles, the Pt/TiO₂/Ti electrocatalyst has a larger active surface area as compared to the Pt/C and Pt/Ti electrocatalysts. Meanwhile the Pt/TiO₂/Ti electrocatalyst displays much better catalytic activity and higher stability for the ethanol electrooxidation in both acidic and alkaline media than the Pt/C and Pt/Ti electrocatalysts as a result of synergistic effect of Pt nanoparticles and the TiO₂ support. The results suggest a promising application of the Pt/TiO₂/Ti electrocatalyst in DEFCs.

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