



# The enhancement effect of nitrogen, fluorine-codoped titanium dioxide on the carbon supported platinum nano-catalyst for methanol electrooxidation reaction



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## H I G H L I G H T S

- N,F–TiO<sub>2</sub> was synthesized by a simple solid state route.
- The addition of N,F–TiO<sub>2</sub> accelerated the oxidative removal of intermediate poison species such as CO.
- Methanol electrooxidation activity and stability on Pt–N,F–TiO<sub>2</sub>/C catalyst were improved.
- The promotion effect should be attributed to the presence of N,F–TiO<sub>2</sub>.

## A R T I C L E I N F O

### Article history:

Received 11 September 2014

Received in revised form

10 November 2014

Accepted 25 November 2014

Available online 26 November 2014

### Keywords:

Direct methanol fuel cells

Methanol electrooxidation

Platinum nanoparticles

Nitrogen

Fluorine-codoped titanium dioxide

Metal–support interaction

## A B S T R A C T

TiO<sub>2</sub> (anatase) codoped with nitrogen and fluorine is synthesized by a simple solid state route, using urea and ammonium fluoride as sources of nitrogen and fluorine, respectively. N,F–TiO<sub>2</sub> and carbon are mixed up physically as hybrid support of Pt nanoparticles for methanol electrooxidation. TEM shows that the utilization of the hybrid support leads to the uniform distribution and small particles size of Pt nanoparticles (Pt NPs) in Pt–N,F–TiO<sub>2</sub>/C catalyst. CO<sub>ad</sub> stripping experiment results indicate that the addition of N,F–TiO<sub>2</sub> facilitates the oxidative removal of CO on Pt surface. Furthermore, cyclic voltammetric and chronoamperometric experiments show that the prepared Pt–N,F–TiO<sub>2</sub>/C catalyst exhibits much better catalytic activity and stability compared to Pt–TiO<sub>2</sub>/C, Pt/C (JM) and Pt/C (hm) catalysts. For instance, the peak current and the stable current at 7200 s of the Pt–N,F–TiO<sub>2</sub>/C catalyst are about 1.85 and 2.66 times of the Pt/C (JM) catalyst. The catalytic performance of the Pt–N,F–TiO<sub>2</sub>/C is also evaluated in a direct methanol fuel cell (DMFC), which exhibits a maximum power density of 51.6 mW cm<sup>−2</sup>, 1.65 times of an analogs fuel cell using Pt/C (JM) as an anode catalyst. Therefore, the N,F–TiO<sub>2</sub> has great application prospect as a high-performance electrocatalyst support for methanol electrooxidation in DMFC.

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## 1. Introduction

Direct methanol fuel cells (DMFCs) are considered to be the promising candidates for portable devices and vehicle applications due to their high energy density, easy manipulation and high efficiency [1–3]. The state-of-the-art DMFCs employ Pt as the anode

catalyst for the electrooxidation of methanol [4–6]. However, the low catalytic activity and stability of this catalyst for methanol electrooxidation are the major obstacles for the commercialization of DMFCs. The low performance of Pt catalyst can be ascribed to several reasons including the low intrinsic activity of Pt, the CO poisoning effect, the weak interactions between Pt and carbon support, the dissolution of Pt element, and electrochemical corrosion of the carbon support [7]. The introduction of an earth-abundant and non-precious co-catalyst is an effective approach to improve the catalytic activity and durability as well as to lower the cost of Pt-based catalysts [5,8]. One approach is to introduce novel

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materials, such as SnO<sub>2</sub> [9,10], WO<sub>x</sub> [11,12], MoO<sub>x</sub> [13,14], and CeO<sub>2</sub> [15,16], as supports. Another way is to dope the carbon support with main group elements such as P [17] and N [18]. To date, the unique physical and chemical properties of TiO<sub>2</sub> [19,20] have attracted increasing attention as an alternative catalyst support due to its excellent mechanical property and stability in acidic and oxidative environments. There have been many reports using TiO<sub>2</sub> as support of Pt or PtRu for methanol electrooxidation [21,22]. However, TiO<sub>2</sub> has some shortcomings such as the poor electrical conductivity and low surface area [23]. It seems practical to combine TiO<sub>2</sub> and carbon to make hybrid support for Pt-based catalysts to overcome these shortages. In the same time, efforts have been made in doping TiO<sub>2</sub> with some metal elements (Fe [24], Ag [25], Nb [26,27], etc.) or non-metal elements (N [28,29], S [30], etc.) to refine the electronic structure of TiO<sub>2</sub>, thereby increasing the catalytic activity of the supported Pt catalysts. Therefore, an excellent catalytic performance for methanol electrooxidation can be expected by using the hybrid support material.

In this paper, we report that N,F-codoped TiO<sub>2</sub> mixed carbon can be used as the support of Pt catalyst for methanol electrooxidation and effectively improve the activity and stability of Pt catalyst. In our work, we treated TiO<sub>2</sub> by a simple solid state route to synthesize N,F–TiO<sub>2</sub> [29] and investigated the effect of N,F–TiO<sub>2</sub> on Pt/C catalyst for methanol electrooxidation. This Pt–N,F–TiO<sub>2</sub>/C catalyst was characterized by X-ray diffraction, X-ray photoelectron spectroscopy, Energy dispersive X-Ray spectroscopy, Transmission electron microscope and electrochemical measurements, compared with the Pt–TiO<sub>2</sub>/C and Pt/C (hm) catalysts prepared in the similar way. It was found that Pt–N,F–TiO<sub>2</sub>/C catalyst exhibited both excellent catalytic activity and stability for methanol electrooxidation. Moreover, the single fuel cell results confirmed the enhancement in fuel cell performance with Pt–N,F–TiO<sub>2</sub>/C as an anodic catalyst.

## 2. Experimental

### 2.1. Chemicals and materials

The hydrophilic anatase TiO<sub>2</sub> was from Aladdin Company. The urea and ammonium fluoride were purchased from Sinopharm Chemical Reagent Co. The chemical reagent H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O and 5 wt % Nafion ionomer were purchased from Aldrich Chemical Co. The Vulcan Carbon powder XC-72 was purchased from Cabot Corporation (USA). Ethylene glycol and NaOH were purchased from Beijing Chemical Co. and were used as received without further purification. Commercial state-of-the-art 20 wt% Pt/C (Johnson Matthey Company, HiSPEC™ 3000) was used as the benchmark for comparison and was denoted as Pt/C (JM). It should be noted that all solutions in our work were prepared using Millipore-MilliQ water (resistivity:  $\rho \geq 18 \text{ M}\Omega \text{ cm}^{-1}$ ) and the reagents used were analytical-grade.

### 2.2. Samples preparation

#### 2.2.1. Preparation of N,F–TiO<sub>2</sub>

Firstly, the commercial TiO<sub>2</sub> (denoted as TiO<sub>2</sub>–C) powder was grounded with excess of urea and NH<sub>4</sub>F (10 times each by weight). After that, the solid mixture was transferred to a tubular oven at 500 °C under the protection of Ar for 2 h (the temperature was ramped at a rate of 5 °C min<sup>-1</sup> to the final treatment and the flow of Ar is 80 cc min<sup>-1</sup>) to obtain the yellow N,F-codoped TiO<sub>2</sub> (denoted as N,F–TiO<sub>2</sub>) powder.

#### 2.2.2. Catalyst preparation

Pt–N,F–TiO<sub>2</sub>/C catalyst (20 wt% Pt, 16 wt% N,F–TiO<sub>2</sub>) was prepared by microwave-assisted polyol reduction method. Firstly, 32 mg Vulcan XC-72 carbon black and 8 mg N,F–TiO<sub>2</sub> were ultrasonically suspended in 40 mL ethylene glycol for 2 h to form a uniform suspension and then aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> was added into the suspension under stirring. After the mixture was stirred vigorously for 4 h, the pH was adjusted to 10 with 1 M NaOH solution under stirring. After that, the mixture was placed in the center of microwave oven (2450 MHz, 750 W) and heated for 90 s, following by stirring for another 8 h. The reaction solutions were filtered and washed with distilled water until no Cl<sup>-</sup> was detected. At last, the obtained catalyst was dried in a vacuum oven at 60 °C overnight. The preparation method of Pt–TiO<sub>2</sub>/C and homemade Pt/C (denoted as Pt/C (hm)) catalysts was similar to that mentioned above.

### 2.3. Physical characterization

The X-ray diffraction (XRD) patterns of the catalysts were obtained using a Rigaku-D/MAX-PC2500 X-ray diffractometer (Japan) with the Cu K $\alpha$  (1  $\frac{1}{4}$ 1.5405 Å) as a radiation source operating at 40 kV and 200 mA. X-Ray photoelectron spectroscopy (XPS) was recorded on a Kratos XSAM-800 spectrometer with an Al K $\alpha$  monochromatic source. The C 1 s peak was used as a reference. Kratos XSAM-800 spectrometer with an Al K $\alpha$  monochromatic source. The composition of catalysts was estimated by Energy dispersive X-ray analysis (EDX) on a JEOL JAX-840 scanning electron microscope operating at 20 kV. The size and morphology of the catalysts were measured by Transmission electron microscope (TEM) analysis carried out with a JEOL2010 microscope operating at 200 kV with nominal resolution. Samples were firstly ultrasonicated in alcohol for 1 h and then deposited on 3 mm Cu grids.

### 2.4. Electrochemical measurements

Electrochemical measurements were carried out with a Princeton Applied Research Model273 Potentiostat/Galvanostat and a conventional three electrode electrochemical cell. A Pt plate was used as the counter electrode. The saturated calomel electrode (SCE) was used as the reference electrode. All of the potentials in this study were reported with respect to SCE unless otherwise mentioned. The glassy carbon electrode was polished with slurry of 0.3 mm and 0.05 mm alumina successively and washed ultrasonically in deionized water prior to use. The working electrode was prepared as follows, firstly, 5 mg of the catalyst was dispersed ultrasonically in 1050  $\mu$ L solutions containing of 1 mL alcohol solution and 50  $\mu$ L Nafion solution, secondly, 5  $\mu$ L catalyst inks were pipetted and spread on the glassy carbon disk with 4 mm diameter. At last, the electrode was obtained after the solvent volatilized with the loading was 0.038 mg cm<sup>-2</sup> Pt.

All electrochemical measurements were carried out in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution with or without 1.0 M CH<sub>3</sub>OH deaerated by pure N<sub>2</sub> for at least 20 min prior to any measurements. For the electrooxidation of methanol, the scan potential range was from -0.2 to +1.0 V. The CO stripping voltammograms were measured in the 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. CO was purged into the 0.5 M H<sub>2</sub>SO<sub>4</sub> solution for 20 min to allow the complete adsorption of CO onto the catalyst when the working electrode was kept at 0 V and then excess CO in the electrolyte was removed by purging N<sub>2</sub> for 20 min at flow rate of ca. 100 mL min<sup>-1</sup>. All the measurements were carried out at room temperature unless otherwise noted. The surface area of Pt metal was estimated assuming that the coulombic charge necessary for oxidation of a monolayer of linearly adsorbed CO was 420  $\mu$ C cm<sup>-2</sup> [31].

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