



# Titanium dioxide encapsulated in nitrogen-doped carbon enhances the activity and durability of platinum catalyst for Methanol electro-oxidation reaction



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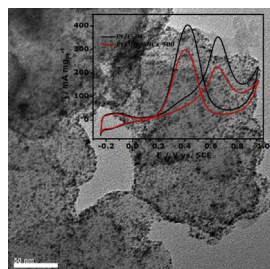
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## HIGHLIGHTS

- TiO<sub>2</sub>@NC<sub>x</sub> was synthesized by pyrolysing polypyrrole and TiO<sub>2</sub> composite.
- Pt/TiO<sub>2</sub>@NC<sub>x</sub> catalysts exhibit high activity and stability towards MOR.
- The high activity in MOR was due to the bifunctional mechanism and electronic effect.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 3 March 2015

Received in revised form

30 April 2015

Accepted 12 May 2015

Available online 19 May 2015

### Keywords:

TiO<sub>2</sub>

Nitrogen doped-carbon

Support material

Methanol oxidation reaction

## ABSTRACT

The development of advanced catalyst supports is a promising route to obtain active and durable electrocatalysts for methanol electro-oxidation reaction. In the current work, nitrogen-doped carbon encapsulated titanium dioxide composite (TiO<sub>2</sub>@NC<sub>x</sub>) is constructed and serves as support material for the Pt catalyst. The TiO<sub>2</sub>@NC<sub>x</sub> support is fabricated by the procedure of an in-situ polymerization and subsequent pyrolysis. The synthesized Pt/TiO<sub>2</sub>@NC<sub>x</sub> catalysts show enhanced electrocatalytic performance towards methanol electro-oxidation compared with the commercial Pt/C catalyst. The enhancement can be ascribed to combinatory effect of N-doped carbon and TiO<sub>2</sub>, in which the tolerance to CO-poisoning and the intrinsic kinetics of methanol oxidation reaction are simultaneously improved by the bifunctional mechanism and the electronic effect. As a result, the as-developed TiO<sub>2</sub>@NC<sub>x</sub> composite is a promising catalyst support material for the application in fuel cell.

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## 1. Introduction

Owing to its high energy density, high energy conversion efficiency and low pollutant emissions, the direct methanol fuel cell (DMFC) is regarded as a promising power source for automotive, portable or stationary systems [1–5]. However the insufficient catalytic activity and durability are key barriers to the commercial deployment of DMFCs [6]. To address this need, an intriguing new

research direction focuses on the development of advanced support material on which the noble metal catalysts are immobilized, which is based on the fact that the chemistry of a support surface can exert an appreciable influence on the behavior of the overlying nanoparticles (NPs). TiO<sub>2</sub> materials as a kind of catalyst support have received increasing attention because of their inherent stability in an electrochemical environment, beneficial interactions with metal catalysts and proton conductivity [7–11]. However, its low electric conductivity and surface area inhibit its applications in fuel cells. To address these shortcomings, strategies including the doping of TiO<sub>2</sub> [12,13], formation of TiO<sub>2</sub>/C composites [14], and construction of nanostructured TiO<sub>2</sub> [15] have been applied to improve their electric conductivity and/or surface area. On the other hand, recent observations suggest that carbon-based support materials can be purposely doping-treated to create strong, beneficial catalyst–support interactions, thereby substantially enhancing catalytic activity and stability of the supported catalyst.

In this work, TiO<sub>2</sub> encapsulated in N-doped carbon (TiO<sub>2</sub>@NC<sub>x</sub>) was synthesized by in situ polymerization pyrrole on TiO<sub>2</sub> and then processed by a high-temperature pyrolysis at various temperatures. The Pt/TiO<sub>2</sub>@NC<sub>x</sub> catalyst was synthesized by a facile microwave-assisted polyol process and exhibited a much enhanced electrocatalytic performance compared to a commercial Pt/C catalyst for methanol oxidation reaction (MOR).

## 2. Experimental

### 2.1. Materials

The hydrophilic anatase TiO<sub>2</sub> was purchased from Aladdin Company. The as-received pyrrole was purified by reduced pressure distillation and preserved in an ampoule bottle. 5 wt% Nafion ionomer was obtained from Aldrich. 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. Ethylene glycol, H<sub>2</sub>SO<sub>4</sub>, and NaOH were purchased from the Shanghai Chemical Factory (Shanghai, China) and were used as received without further purification. Ultrapure water (Millipore, 18.2 MΩ cm) was used throughout all experiments.

### 2.2. Catalysts synthesis

#### 2.2.1. Synthesis of TiO<sub>2</sub>@NC<sub>x</sub> supports

Polypyrrole/titanium dioxide (PPy/TiO<sub>2</sub>) complex was synthesized by an oxidation polymerization process. Typically, 0.02 mol pyrrole and 0.002 mol TiO<sub>2</sub> were added into 50 ml H<sub>2</sub>SO<sub>4</sub> solution (1 mol L<sup>-1</sup>) and ultrasonically dispersed to form pyrrole/titanium dioxide suspension. Then 50 ml pre-cooled ammonium persulfate (APS) solution (0.005 mol APS in 50 ml 1 M L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution) was added and the suspension was kept stirring for 24 h at room temperature. The products were then filtrated and rinsed with large amount of deionized water. Finally, the obtained PPy/TiO<sub>2</sub> was pyrolyzed in a nitrogen atmosphere for 3 h with a heating rate of 5 °C per minute to form the N-doped carbon coated TiO<sub>2</sub> support (TiO<sub>2</sub>@NC<sub>x</sub>). And the products were denoted as TiO<sub>2</sub>@NC<sub>x</sub>-T (T represents the pyrolyzed temperature, eg. 700, 800, 900 and 1000 °C).

#### 2.2.2. Synthesis of Pt/TiO<sub>2</sub>@NC<sub>x</sub> catalysts

Pt/TiO<sub>2</sub>@NC<sub>x</sub> catalysts with 20% Pt loading were synthesized by a microwave-assisted polyol method in ethylene glycol solution. Typical synthesis procedure is as follows: 50 mg TiO<sub>2</sub>@NC<sub>x</sub> was suspended in 40 ml ethylene glycol and ultrasonic dispersed for 1 h. Then, 893 μL of chloroplatinic acid (14 mg mL<sup>-1</sup>) in 10 ml ethylene

glycol was added and the pH of the suspension was adjusted to 10 with 0.1 M NaOH aqueous solution. Subsequently, the suspension was subjected to consecutive microwave heating for 90 s. After microwave radiation the resulting solution was stirring for another 8 h before filtrating, washing with alcohol and distilled water. Finally, the material was dried at 80 °C in a vacuum oven for 8 h and obtained the Pt/TiO<sub>2</sub>@NC<sub>x</sub>-T catalyst.

### 2.3. Physical characterizations

Scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and element mapping analysis were conducted on a XL30 ESEM FEG field emission scanning electron microscope operating at 20 kV. Transmission electron microscopy (TEM) and High resolution transmission electron microscopy (HRTEM) were used to analyze the size and morphology of catalysts on a Philips TECNAI G2 operating at 200 KV. Raman spectra were collected on a J-Y T64000 Raman spectrometer with 514.5 nm wavelength incident laser light. The X-ray diffraction (XRD) patterns of the catalysts were obtained using a PW1700 diffractometer (Philips Co.) with a Cu Kα (λ = 0.15405 nm) radiation source operating at 40 kV and 30 Ma. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos XSAM-800 spectrometer with an Mg Ka radiation source.

### 2.4. Electrochemical measurements

All electrochemical measurements were carried out with an EG&G mode 273 potentiostat/Galvanostat and a conventional three-electrode test cell at the ambient temperature. A glassy carbon disk coated with catalyst was used as the working electrode. The counter-electrode and reference-electrode were a Pt foil and a saturated calomel electrode (SCE) respectively. The glassy carbon disk was polished with 0.3 and 0.05 μm alumina powder, sonicated and rinsed with deionized water before used. The homogeneous catalyst ink was prepared by ultrasonically dispersing the mixture of 5 mg catalyst, 950 μL ethanol, and 50 μL Nafion alcohol solution (Aldrich, 5 wt% Nafion) for 30 min. Next, 5 μL catalyst ink was pipetted and spread on a 3 mm-diameter pre-cleaned glassy carbon disk as the working electrode. All electrolyte solutions were deaerated by high-purity nitrogen for at least 15 min prior to any measurement. To evaluate the catalytic activity for methanol, the cyclic voltammetry experiments were carried out in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M CH<sub>3</sub>OH solution with a scan rate of 50 mV s<sup>-1</sup>. The chronoamperometry experiments were performed in the same solution at the potential of 0.5 V (vs.SCE) for 3600 s.

## 3. Results and discussion

### 3.1. Characterization of the TiO<sub>2</sub>@NC<sub>x</sub> support

SEM was used to observe the changes in the morphology of the TiO<sub>2</sub>@NC<sub>x</sub> supports as a function of heat-treatment temperature. As shown in Fig. 1a, the as-prepared PPy/TiO<sub>2</sub> composite presented a well-defined sphere-like morphology with a diameter of ~200 nm. After pyrolysis at 700 °C for 3 h, the size of the nanosphere reduced compared to that of the PPy/TiO<sub>2</sub>, demonstrating that the nanosphere-like structure was destroyed and carbonization occurred during the pyrolysis process. The size of nanosphere decreased with increasing temperature until 900 °C. When the temperature increased to 1000 °C, the morphology for TiO<sub>2</sub>@NC<sub>x</sub>-1000, however, featured large agglomerated particles, resulting in a disadvantageous impact on the overall surface area and porosity. The SEM image of the Pt/TiO<sub>2</sub>@NC<sub>x</sub>-900 catalyst was also obtained to probe the morphology changes after Pt loading. As shown in

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