



Research Paper

Advanced architecture carbon with in-situ embedded ultrafine titanium dioxide as outstanding support material for platinum catalysts towards methanol electrooxidation



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ABSTRACT

Here we report a novel Pt catalysts support material, i.e. the resorcinol-formaldehyde (RF) resin derived carbon embedded titanium dioxide (TiO₂@RFC) with well-tuned pore structure and excellent electrical conductivity. The material is synthesized by in-situ polymerization of RF gel with porous texture at the presence of TiO₂, followed by high temperature pyrolysis. The Pt nanoparticles (NPs) are deposited on the composites carbon material to form the methanol electrooxidation catalysts in direct methanol fuel cells (DMFCs). The optimized Pt/TiO₂@RFC catalyst possesses a comparably high electrochemical active surface area of 71.6 m² g⁻¹ (68.3 m² g⁻¹ for commercial Pt/C), attributed to its smaller Pt NPs size (2.62 nm) than the commercial Pt/C (2.84 nm). The maximum current densities during methanol electrooxidation reaction (MOR) for the optimized Pt/TiO₂@RFC (822.2 mA mg⁻¹) is 1.4 times higher than commercial Pt/C (344.4 mA mg⁻¹). Remarkably, after accelerated degradation test through 2000 cyclic voltammetry, the mass activity for Pt/TiO₂@RFC was well maintained at 689.5 mA mg⁻¹, 3.3 times that of the commercial Pt/C (206.1 mA mg⁻¹, decline of 40.17%). The sustainable electro-catalytic stability of Pt/TiO₂@RFC for MOR may be ascribed to the unique structure and composition of the supported material, which provides a strong metal-support interaction and significantly suppresses the degradation processes in the long-term cyclic measurements.

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1. Introduction

Direct methanol fuel cells (DMFCs) have drew far-ranging research attentions in recent decades, which are featured of simple construction, high energy density & conversion efficiency, as well as low operating temperature and environmentally benign quality. These properties are considered as indispensable to a large amount of applications, such as portable electronics, electric vehicles, and public transportation [1–3]. Unfortunately, though Pt is recognized as the ideal element for methanol oxidation reaction (MOR), its high cost is still one of the major obstacles in impelling DMFCs to practical application [4–8]. Additionally, Pt degrades in both the electrocatalytic activity and utilization during the running course of fuel cells [9,10]. Thus, overcoming issues including metal

particles agglomeration, detachment and dissolution are of vital importance for DMFCs [11–13]. Much efforts have been devoted through the following two approaches: one is to decrease the size of particles, to bring about the increase of electrochemical active surface areas (ECSAs) [14–16]; the other is to introduce other metals or supports to Pt to decorate the electronic structure on catalysts' surface, which is beneficial to enhance the performance and durability for MOR [17–21].

The support-catalysts interaction plays an important role in the noble metal catalysis [22–28]. The supports are regarded as the substrate material to increase the metal catalysts dispersion and simultaneously decorate the chemical/electronic structure to regulate the electrocatalytic performance. Carbon supported Pt-based catalysts are deemed as the state-of-the-art catalysts for fuel cells related reactions including both fuel oxidations (H₂ and small organic molecules) and oxygen reduction reaction. However, these kinds of electrocatalysts are confused by the deficiency of long-term durability, which limits their practical applications [29–31].

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Recently, a great deal of research efforts have been centered on the development of stability by confining/encapsulating Pt with porous carbon [32]. Maiyalagan et al. have encapsulated metal nanoparticles, such as Pt and PtRu, into CMK-8 with 3D bi-interpenetrating channels, which acquired prominent specific activity and outstanding stability [33]. Yang et al. confined Pt and PtRu NPs in hollow core-mesoporous shell carbon sphere structure by SiO₂ template method and obtained catalysts with remarkable stability [34,35]. The above literature indicated that the method embedding metal particles into the pore channels of a meso-structured carbon effectively improves the catalyst stability. However, these structures may sacrifice some Pt active sites in MOR, which decrease the utilization ratio of noble metal.

To address these problems, we introduce TiO₂ particles to the carbon support. TiO₂ is usually regarded as a potential catalyst support because of its more inherent stability in electrochemical environment, more beneficial interactions with noble metal catalysts, and higher proton conductivity compared to the other oxides, while its poor electric conductivity and low surface area inhibits its application in fuel cells [36–38]. Herein, a simple method to embed TiO₂ into resorcinol-formaldehyde (RF) resin derived carbon is developed, which is synthesized through in situ polymerization at the presence of TiO₂, followed by programmed calcination at high temperature. The composite exhibits an extra-large specific surface area and desirable pore structural tuned by in-situ embedded TiO₂. The novel catalyst architecture, on the one hand, enhances the electrocatalytic stability in methanol oxidation process; on the other hand, decreases the particle size of Pt due to optimized metal-support interaction. Compared with commercial Pt/C catalysts, the as-prepared Pt/TiO₂@RFC electrocatalysts exhibited ultrahigh catalytic stability in MOR, outstanding electrocatalytic activity, and higher CO tolerance.

2. Experimental

2.1. Synthesis of TiO₂@resorcinol-formaldehyde resin carbon (TiO₂@RFC) and TiO₂ + RFC-20% supports

The TiO₂@RFC was synthesized by heating mixtures of resorcinol-formaldehyde resin (a carbon precursor) and anatase TiO₂ NPs (5–10 nm, hydrophilic). The preparation process of the support materials was similar with our previous works [39]. The detailed flow was shown in Fig. 1a: the mixture containing a certain amount of Na₂C₂O₄, m₁ TiO₂ powder (m₁ equals to 5, 11, 26 mg ml⁻¹, which was represented as a, b, c respectively) and 1.2234 g resorcinol were dispersed in 20 ml distilled deionized water and magnetically stirred for 30 min. The solution was heated to T₁ = 94 °C while 1.640 ml aqueous formaldehyde solution was

added and stirred under reflux. After 48 h, the suspension was vacuum-dried at room temperature and milled to obtain a TiO₂@resorcinol-formaldehyde resin powder. Finally, the TiO₂@resorcinol-formaldehyde resin was heated at T₂ = 900 °C for 3 h in an Ar gas atmosphere. Afterward, the TiO₂@RFC was obtained after being ground into a powder and washed with deionized water.

2.2. Synthesis of the Pt based catalysts deposited on different supports materials

Pt based catalysts with a Pt loading of 20 wt. % were synthesized through a process with ethylene glycol as the reducing agent [40]. Firstly, 20 mg of TiO₂@RFC (TiO₂ + RFC or RFC) was suspended in 20 ml of an ethylene glycol solution, and a 332 μL H₂PtCl₆ solution (15.067 mg_{Pt} mL⁻¹) was added. Then, the mixture was heated at 150 °C for 3 h. Subsequently, the suspension was filtered and washed with deionized water and then dried at 60 °C for 10 h to obtain the Pt/TiO₂@RFC catalysts. And the structural features of Pt/TiO₂@RFC and Pt/TiO₂ + RFC-20% was shown in Fig. 1b.

2.3. Physical characterizations

Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (STEM) and element mapping analysis were conducted on a TECNAI G2 operating at 200 kV.

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.

X-Ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos XSAM-800 spectrometer with an Mg Kα radiation source.

X-Ray diffraction (XRD) measurements were performed with a PW1700 diffract meter (Philips Co.) using a Cu Kα (λ = 0.15405 nm) radiation source. The obtained XRD patterns were analyzed with Jade 5.0 software to remove the background radiation.

The textural and morphological features of the different carbon supports and catalysts prepared were determined by means of nitrogen physisorption at 77 K in a Quantachrome Autosorb-iQ. Textural properties such as specific surface area, pore volume, and pore size distribution were calculated from each corresponding nitrogen adsorption-desorption isotherm applying the Brunauer-Emmet-Teller (BET) equation and Barrett-Joyner-Halenda (BJH) and density function theory (DFT) methods in ASiQwin 3.01 program.

2.4. Electrochemical measurements

Electrochemical measurements were carried out with an EG&G mode 273 potentiostat/galvanostat in a conventional three electrode test cell. The catalyst ink was prepared by ultrasonically dispersing a mixture containing 5 mg of catalyst, 950 μL of ethanol and 50 μL of 5 wt % Nafion solution. Next, 10 μL of the catalyst ink was pipetted onto a pre-cleaned glassy carbon disk (diameter = 5 mm) (polish with 0.3 and 0.05 mm alumina powder, sonicated and rinsed with deionized water) as the working electrode. A Pt foil and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively. All of the potentials are relative to the SCE electrode, unless otherwise noted. In order to activate and clean the catalyst surface, the working electrodes were potentially cycled from -0.2 V and 0.958 V at a scan rate of 50 mV s⁻¹ in 0.5 M H₂SO₄ solution until a stable response was obtained. To evaluate the activity of the catalysts for methanol oxidation reaction (MOR), cyclic voltammetry (CV) measurements were performed at room temperature between -0.2 V and 0.958 V

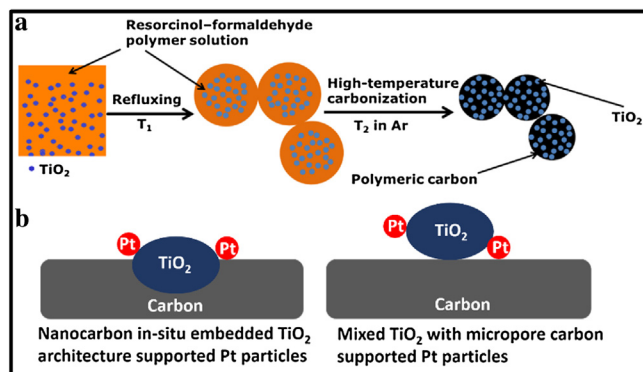


Fig. 1. Illustrative drawings of the TiO₂@RFC formation (a) and of the structural features of Pt/TiO₂@RFC (b, left) and Pt/TiO₂ + RFC (b, right).

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