



TiN@nitrogen-doped carbon supported Pt nanoparticles as high-performance anode catalyst for methanol electrooxidation



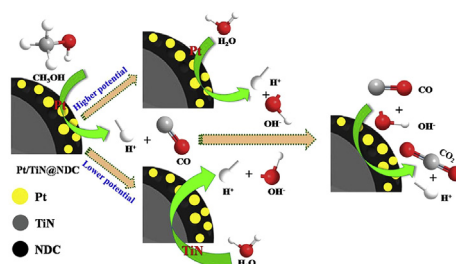
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HIGHLIGHTS

- Pt/TiN@NDC catalyst has been successfully prepared.
- Pt NPs are uniformly dispersed in TiN@NDC surface with a narrow distribution.
- A strong metal-support interaction is existed between Pt and TiN@NDC support.
- Pt/TiN@NDC catalyst exhibits the highest ECSA and catalytic activity toward MOR.
- The novel Pt/TiN@NDC catalyst reveals a better CO tolerance.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, TiN@nitrogen-doped carbons (NDC) composed of a core-shell structure are successfully prepared through self-assembly and pyrolysis treatment using γ -aminopropyltriethoxysilane as coupling agent, polyaniline as carbon and nitrogen source, respectively. Subsequently, TiN@NDC supporting Pt nanoparticles (Pt/TiN@NDC) are obtained by a microwave-assisted polyol process. The nitrogen-containing functional groups and TiN nanoparticles play a critical role in decreasing the average particle size of Pt and improving the electrocatalytic activity of Pt/TiN@NDC. Transmission electron microscope results reveal that Pt nanoparticles are uniformly dispersed in the TiN@NDC surface with a narrow particle size ranging from 1 to 3 nm in diameter. Moreover, the Pt/TiN@NDC catalyst shows significantly improved catalytic activity and high durability for methanol electrooxidation in comparison with Pt/NDC and commercial Pt/C catalysts, revealed by cyclic voltammetry and chronoamperometry. Strikingly, this novel Pt/TiN@NDC catalyst reveals a better CO tolerance related to Pt/NDC and commercial Pt/C catalysts, which due to the bifunctional mechanism and strong metal-support interaction between Pt and TiN@NDC. In addition, the probable reaction steps for the electrooxidation of CO adspecies on Pt NPs on the basis of the bifunctional mechanism are also proposed. These results indicate that the TiN@NDC is a promising catalyst support for methanol electrooxidation.

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1. Introduction

Over the past few decades, fuel cells have been extensively studied as promising power sources because of the depletion of fossil fuels and rising environmental pollution [1]. As an ideal energy source for electric vehicles and portable electronics, direct

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methanol fuel cells (DMFCs) have received broad attention due to their high energy density, safe for storage and transportation, fast start-up and low operating temperature [2,3]. However, major shortcomings hindering the successful application of DMFCs are low activity and serious CO poisoning of Pt-based catalysts. Therefore, the study of the electrooxidation of CO becomes necessary, not only for a practical purpose but also for fundamental science. Until recently, sufficient efforts have been devoted to the synthesis of Pt-based alloys catalysts such as Pt-Pb [4], Pt-Bi [5], Pt-Mn [6], Pt-Zn [7], Pt-Ni [8], Pt-Au [9], Pt-Rh [10], Pt-Cu [11], Pt-Co [12] and Pt-Ru [13]. As of now, Pt-Ru alloyed nanoparticles (NPs) remains the start-of-the art electrocatalyst for MOR based on bifunctional mechanism and electronic ligand effect mechanism [14–16]. However, the most commonly used Pt-Ru catalyst is controlled by the high cost and global reserves, additionally, a considerable part of the performance loss is due to the leaching of Ru during extended operation and repeated cycling [17,18]. Therefore, one of the principal tasks of DMFCs is developing an alternative catalyst support materials with excellent catalytic activity and high durability.

Currently, metal oxides and nano-ceramic materials, such as TiO₂ [19], Ti₄O₇ [20], Al₂O₃ [21], SnO₂ [22], Fe₃O₄ [23], WO₃ [24], WN [25], ZrO₂ [26], CeO₂ [27], RuO₂ [28], TiC [29] and TiN [30] have been reported to be a promising support materials for fuel cell to enhance catalytic activity and stability. Of the various types of supports, TiN has been explored as an ideal supports in oxygen reduction reaction [31], polymer electrolyte fuel cells [32–34] and DMFCs [35–38] because it has highly electrically conductive, thermally stable with exceptional hardness, and corrosion resistant under fuel cell operating conditions. What is more, the presence of TiN would help the formation of Ti-OH type functional groups at low over potentials by dissociating water which in turn help in alleviating the CO intermediate species formed during the oxidation of methanol on Pt sites [18,39]. Catalysts composed of Pt on TiN materials have been reported to exhibit improved catalytic activity for methanol oxidation and enhanced CO tolerance as well as durability [39–46]. Nevertheless, Avasarala et al. has been reported that potential cycling of TiN NPs in perchloric acid will passivate the surface and reduce its electrical conductivity thereby inhibiting electron transportation in Pt/TiN electrocatalysts [35,47].

Typically, carbon is the most widely used material for supporting nanosize metallic particles in the electrode for DMFCs. Watanabe et al. have reported the catalytic qualities can be improved by mixing TiN with carbon black as an electron-conducting path in the catalyst layer [48]. Recently, much work focused on the nitrogen-doped carbon (NDC) materials with N species incorporated into carbon matrix to promote the catalyst performance of DMFCs due to the following probable reasons: (1) the nitrogenized sites in carbon matrix increase the conductivity for fast transport of electrons [39]; (2) nitrogen doping accelerates the nucleation and growth behavior of Pt NPs and favors to obtain small particles with uniform dispersion [49]; (3) the N functional group sever as binding sites for anchoring Pt NPs to avoid the detachment and agglomeration of the Pt NPs [50]. Our groups have been established a hierarchical nitrogen doped porous hollow carbon spheres supported Pt catalyst and the catalyst exhibited a high conductivity and high dispersion of fine Pt NPs, resulting in the improved catalytic activity and durability toward methanol oxidation reaction (MOR) [51]. In addition, some studies have reported that oxophilic C-N defects, which are generated in nitrogen doped graphitic plane, will be beneficial for dissociation of water to form OH species at low positive potentials [52,53]. Based on the above consideration, one would expect to be able to assemble a TiN@NDC with a core-shell structure supported Pt catalyst (Pt/TiN@NDC) that would exhibit the desirable catalytic qualities of both core-shell structure and

TiN@NDC-supported Pt catalyst according to the bifunctional mechanism.

In the present investigation, the TiN@NDC support consisting of TiN as a core and NDC as a shell was prepared by *in situ* self-assembly method and subsequently carbonized at 900 °C, and then using a microwave-assisted polyol process to deposit Pt NPs on the resulting TiN@NDC supporting materials, as illustrated in Fig. 1. Our testing results show that the Pt/TiN@NDC catalyst exhibit surprisingly high activity and CO tolerance for the MOR in the acidic solution.

2. Experimental

2.1. Materials

Aniline, ammonium peroxydisulfate (APS), sulfuric acid (H₂SO₄), perchloric acid (HClO₄), sodium hydroxide (NaOH), nitric acid (HNO₃), methanol (CH₃OH), ethanol (C₂H₅OH), ethylene glycol (EG), isopropanol and toluene were all purchased from Chuandong Chemical Reagent Company (Chengdu, China). All chemicals used were of analytical grade. γ -aminopropyltriethoxysilane (APTES, 98%) was obtained from Yanxin Chemical Reagent Co., Ltd (Baoji, China). Hexachloroplatinic acid (H₂PtCl₆·6H₂O, 99.9%) was purchased from the First Regent Factory (Shanghai, China). Nafion solution was purchased from Dupont China Holding Co.,Ltd. Titanium nitride (TiN) with particle size of 20 nm was obtained from Chengdu Aike Da Chemical Reagents Co.,Ltd. Commercial Pt/C (E-TEK) catalyst (3.3 nm, 20 wt% Pt supported on Vulcan XC-72R carbon) was used for comparison. Ultrapure water (Millipore, 18.2 M Ω cm) was used throughout all experiments.

2.2. Material preparations

2.2.1. Preparation of APTES grafted TiN NPs

The typical procedure for synthesis of APTES grafted NPs has been described elsewhere. TiN NPs were taken in 100 mL of boiling ultrapure water for 2 h to generate a nanoparticle surface with high coverage of hydroxyl groups. After dried under vacuum overnight, 1.5 g NPs were dispersed into the solution containing 60 mL toluene and 1 g APTES with stirring for 6 h at 110 °C, and then the obtained mixture solution was filtered and washed with ethanol to remove the unreacted APTES. The TiN-APTES NPs were finally dried at 60 °C for 24 h.

2.2.2. Preparation of TiN@NDC support

TiN-APTES@polyaniline (TiN-APTES@PANI) were first synthesized by *in situ* self-assembled method and the typical process consisted of the following steps: 0.2 g TiN-APTES NPs was added to a 250 mL beaker containing 50 mL of 1 M H₂SO₄ solution under ultrasonic treatment for 0.5 h, and then adding 0.3 mL of aniline solution and keep ultrasonic treatment for another 0.5 h. After that, the mixture was stirred for 3 h to form a uniform suspension, 0.74 g of APS in 50 mL of 1 M H₂SO₄ solution was given dropwise within 3 h under stirring to initiate the polymerization, and the above mixture was allowed to polymerize for another 12 h at room temperature. The obtained precipitate was dried in a vacuum oven at 60 °C for 12 h after sufficient filtering and washing with ethanol and ultrapure water to remove oligomers. Finally, the obtained TiN-APTES@PANI was carbonized to get TiN@NDC support in a quartz tube furnace at a heating rate of 5 °C min⁻¹ at 900 °C for 1 h under an argon atmosphere. At the same time, PANI and the corresponding NDC were prepared by the same steps for comparison.

2.2.3. Preparation of Pt/TiN@NDC catalyst

Pt-based catalyst with the Pt loading of 20 wt% was synthesized

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