



Enhanced activity and durability of platinum anode catalyst by the modification of cobalt phosphide for direct methanol fuel cells



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ABSTRACT

In this study, carbon nanotubes (CNTs) supported Pt-cobalt phosphide (CoP) electrocatalyst (Pt/CoP/CNTs) is designed and prepared for methanol oxidation (MOR) for the first time. The modification of CoP decreases the Pt particle size significantly and increases the electrochemical surface areas due to the interaction between Pt and CoP, which is evidenced by transmission electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy. Among all these catalysts, Pt/4%CoP/CNTs catalyst exhibits the best MOR activity of $1600 \text{ mA mg}^{-1} \text{ Pt}$, which is six times that of Pt/CNTs. Moreover, this catalyst also exhibits the higher onset current density and steady current density than the other Pt-based catalysts. The work provides a promising method to develop the highly active and stable Pt-based catalyst for direct methanol fuel cells.

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1. Introduction

Due to the wide application of portable devices, the demands for high energy density and long-term power supply have becoming more and more urgent. The lithium-ion and nickel batteries are hard to fulfill the requirement due to the limited capacity; instead, the direct methanol fuel cells (DMFC) will be a suitable alternative power supply. Pt-based catalysts have low oxidation potential and relatively high activity in methanol oxidation reaction (MOR), as a result, they are the main catalysts for practice application in DMFC. However, the cost of DMFC is high due to the use of Pt as the catalyst active component. Despite the great progress towards non-Pt-based catalysts has been made recently, generally speaking, in proton exchange membrane system, metal-free materials are still not available in MOR, Pt and Pt-alloys are still the most practical catalysts at the current stage of technology [1–3]. To bring down the cost of DMFC, many scientists have dedicated to reduce Pt loading and improve its specific mass activity.

Over the past years, Pt-based nanostructured catalysts have attracted more and more attention, two main strategies for reducing cost and improving performance have been put forward. One strategy is to alloy Pt with another metal, such as Ru, Pd, Ni and Co [4–7], these metals can change the CO adsorption site and

enhance the anti-CO poisoning ability. Another strategy is to decorate Pt using metal oxides, such as RuO_2 , MnO_2 , MoO_2 and IrO_2 [8–11]. The hydration of metal oxides can significantly change the transfer condition of electron and proton, resulting in a change of electrochemical property. All the strategies can significantly improve the activity of Pt catalyst, but the utilization ratio and stability of Pt-based catalysts are still low. Recently, core-shell nanostructures with a monolayer surface of noble metal have been found to offer an enormous possibility for minimizing the amount of Pt needed for catalysis [3], however the complex preparation process makes them hard to fabricate on large-scale. Therefore, it is still the most attractive and long-term research topic in the field of fuel cells to develop the highly stable and active Pt-based catalyst.

Transition metal phosphide is a kind of covalent compounds formed by metal and P [12]. These compounds were widely used as anode materials of lithium ion battery [13], and catalysts in hydrodesulfurization reaction (HDS) [14] and in hydrogen evolution reaction (HER) [15]. HDS and HER involve the bonding process of H^+ , considering that H^+ is also produced by MOR, we expect to use transition metal phosphide to modify Pt catalyst, promoting the activity of MOR. In fact, Chang et al. [16] have reported that the Ni_2P modified Pt catalyst had a high electrochemical activity and stability in MOR. It is well known that CoP is also a common transition metal phosphide, its HDS activity is lower than that of Ni_2P [17], but its HER activity is high and stable [18]. This result inspires us to use CoP instead of Ni_2P to design the CoP modified Pt catalyst. Moreover, carbon nanotubes (CNTs) have been regarded as promising supporting materials of electrocatalyst due to their

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unique structure and excellent conductivity and high stability [19–21]. Herein, Pt/CoP/CNTs catalyst with enhanced activity and stability for MOR has been designed and prepared for the first time, and the effect of CoP on catalytic activity has been discussed.

2. Experimental section

2.1. Preparation and characterization of catalysts

CNTs were provided by Shenzhen Nanotech Port Co., Ltd. Before use, it was treated by a well-known acid oxidation method to introduce oxygenated groups for the subsequent immobilization of Pt. The $\text{Co}_3\text{O}_4/\text{CNTs}$ hybrid was synthesized using a hydrothermal method reported before [18]. In a typical synthesis, the pre-treated 100 mg CNTs were added into 120 mL of ethanol and 2.5 mL of water. After the mixture was sonicated for several minutes, 2.2 mL of 0.5 M $\text{Co}(\text{OAc})_2$ aqueous solution and 2 mL of NH_4OH were added under stirring at room temperature. Then the suspension was kept at 80 °C and stirred for 20 h. After that, the mixture was transferred to 40 mL Teflon-lined autoclaves and maintained at 150 °C for 3 h. After that, the as-prepared product was collected by centrifugation and washed with ethanol and deionized water. The CoP/CNTs were synthesized as follow: 20 mg of $\text{Co}_3\text{O}_4/\text{CNTs}$ and 100 mg of sodium hypophosphite (NaH_2PO_2) were mixed together and grind to a fine powder by using a mortar. Then, the mixture was calcined at 300 °C for 2 h with a heating speed of 2 °C/min. The obtained product was washed with deionized water and dried at 80 °C overnight. The Pt/CoP/CNTs were prepared by ethylene glycol reduction method as follows. The as-prepared CoP/CNTs were added to ethylene glycol under constant stirring for 10 min, and then the appropriate amounts of H_2PtCl_6 and KOH were added. The slurry was refluxed at 140 °C for 2 h to ensure a complete reduction of Pt(IV). The solid product was filtrated and rinsed repeatedly with deionized water. And the solid was dried in vacuum at 70 °C for 12 h.

Carbon nanotube supported PtP catalyst (denoted as PtP/CNTs) was synthesized using a similar method with only a certain amount of H_2PtCl_6 solution and NaH_2PO_2 (Pt: NaH_2PO_2 = 1:60, mole ratio) was added to the suspension [16]. Carbon nanotube supported PtCo catalyst (denoted as PtCo/CNTs) was synthesized by co-impregnation with aqueous solution of H_2PtCl_6 and Co (NO_3)₂, and reduction with KBH_4 [22]. Pt/CNTs were prepared using the ethylene glycol reduction method mentioned in previous work [21]. The Pt loading was 12 wt.% for all the Pt-based catalysts in this paper.

X-Ray diffraction (XRD) measurement was performed with a Bruker2 diffractometer (Bruker Co.) to determine the composition and crystal phase of catalysts. X-Ray photoelectron spectroscopy (XPS) measurement was carried out on a Kratos Axis Ultra DLD spectrometer to determine the surface property of the catalysts. Transmission electron microscopy (TEM) was performed on a JEM-2010HT microscope to determine the morphology of the catalysts. Electro-probe microanalyzer (EPMA, EPMA-1600, Shimadzu Corporation) was used to determine the content of Pt and other element in the catalysts.

2.2. Electrode preparation and electrochemical experiments

The glassy-carbon (GC) electrodes were cleaned by polishing with 0.05 μm alumina powder suspension (water) followed by ultrasonic cleaning in deionized water before use. The catalyst ink was prepared by ultrasonically dispersing a mixture containing 1 mg of catalyst, 385 μL deionized water, 100 μL acetone and 15 μL of a 5 wt.% Nafion solution. 10.0 μL suspension of each catalyst was pipetted onto the glassy carbon electrode surface and the electrode was dried at room temperature for 30 min before measurement. This leads to a catalyst loading of 0.02 mg on GC electrode (0.1256 cm^2).

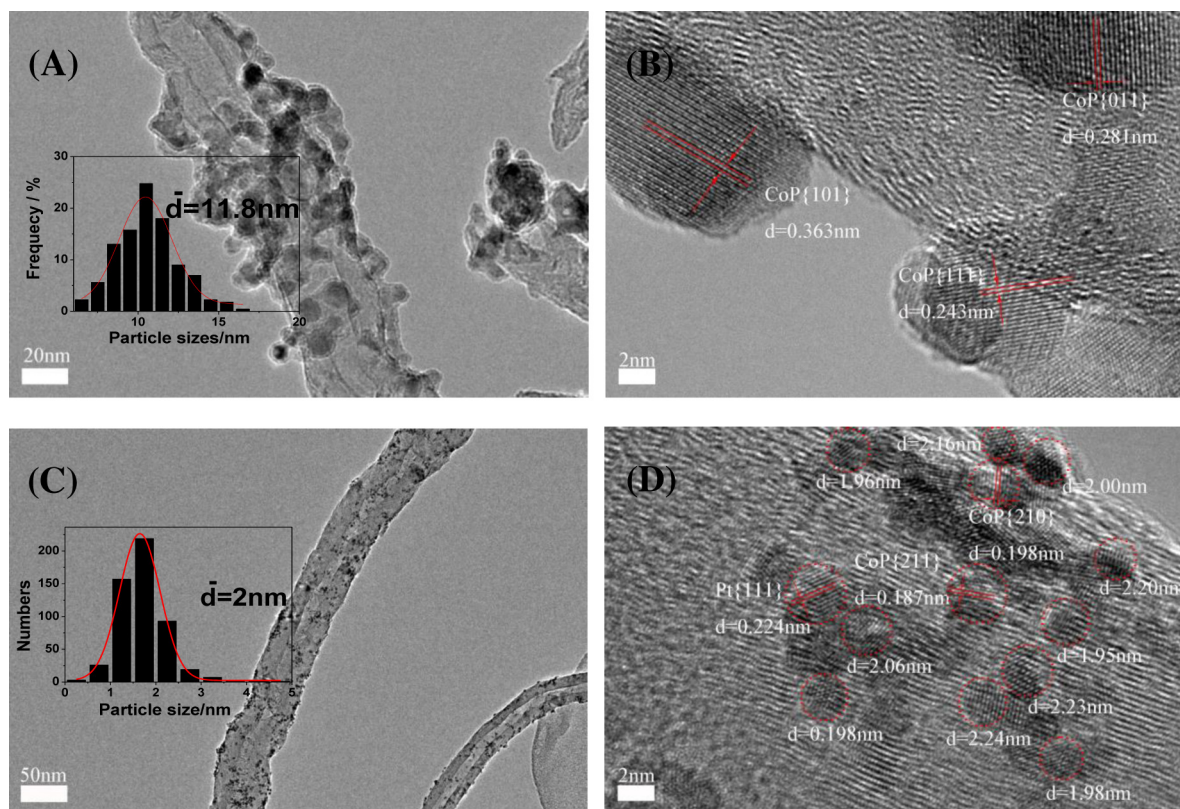


Fig. 1. (A) TEM and (B) HRTEM images of CoP/CNTs, (C) TEM and (D) HRTEM images of Pt/CoP/CNTs. The insets are the corresponding particle size distributions.

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