Journal of Power Sources 300 (2015) 245–253

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Boron-doped graphene as promising support for platinum catalyst with superior activity towards the methanol electrooxidation reaction

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HIGHLIGHTS

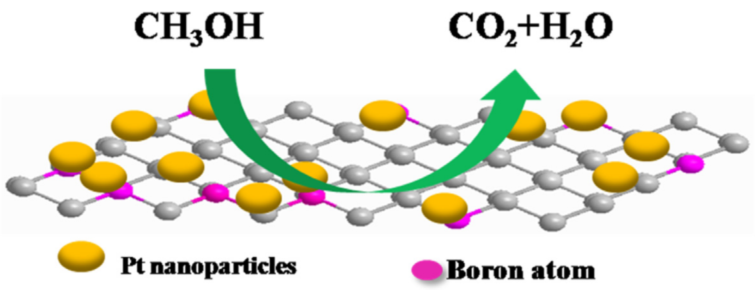
- Boron-doped graphene (BG) was synthesized through thermal annealing.
- BG supported Pt (Pt/BG) catalyst exhibits high activity for the methanol oxidation.
- Low CO adsorption energy contributes to the methanol oxidation activity of Pt/BG.
- Doped boron lowers the d-band center of Pt and weakens CO adsorption.

ARTICLE INFO

Article history:
Received 10 June 2015
Received in revised form
18 August 2015
Accepted 11 September 2015
Available online 28 September 2015

Keywords:
Boron doped graphene
Platinum catalyst support
Methanol electrooxidation
Carbon monoxide tolerance
Stability

GRAPHICAL ABSTRACT



ABSTRACT

We report the synthesis of boron-doped graphene by thermally annealing the mixture of graphene oxide and boric acid, and its usage as the support of Pt catalyst towards the methanol oxidation reaction. The composition, structure and morphology of boron-doped graphene and its supported Pt nanoparticles (Pt/BG) are characterized by transmission electron microscopy, inductively coupled plasma mass spectrometry, Raman spectroscopy, X-ray diffraction and X-ray photoelectron spectroscopy. It is revealed that boron atoms are doped into graphene network in the form of BC_2O and BCO_2 bonds, which lead to the increase in defect sites and facilitate the subsequent deposition of Pt nanoparticles. Therefore, the Pt/BG catalyst presents smaller particle size and narrower size distribution than the graphene supported Pt (Pt/G) catalyst. When evaluated as the electrocatalyst for the methanol oxidation reaction, the Pt/BG catalyst exhibits excellent electrochemical activity and stability demonstrated by cyclic voltammetry and chronoamperometry tests. The enhanced activity is mainly ascribed to the electronic interaction between boron-doped graphene and Pt nanoparticles, which lowers the d-band center of Pt and thus weakens the absorption of the poisoning intermediate CO. Our work provides an alternative approach of improving the reaction kinetics for the oxidation of small organic molecules.

1. Introduction

Direct methanol fuel cells (DMFCs) have been of great research interest as one of the most promising power sources due to their simple structure, ease of operation and high energy density [1,2].

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http://dx.doi.org/10.1016/j.jpowsour.2015.09.046
0378-7753/

However, the slow kinetics of the anodic methanol oxidation reaction (MOR) represents a major problem. Currently, Pt or Pt-based alloy nanoparticles supported on carbon black are the most widely used catalysts for the MOR in DMFCs [3–5]. Unfortunately, their catalytic performance is continuously declined due to the adsorption of the poisoning intermediates formed in the anodic MOR process [6]. CO is confirmed as the main poisoning intermediate during the MOR, which is strongly adsorbed on Pt surface, forming the Pt—CO species that block the active sites for further catalytic reaction. Therefore, the most important strategy for enhancing the MOR activity is to improve the CO tolerance of the anode catalysts. To this end, various Pt alloys, such as PtRu [5], PtFe [7], PtSn [8], PtSnRu [8], PtNi [9], PtAu [10], PtCu [11], PtPd [12] and PtPb [13], have been optimized. Although the activity of these alloys towards the MOR is significantly improved, it is still far from the requirement for the commercialization of DMFCs.

Recently, the development of alternative support materials (e.g. carbon nanotubes [14,15] and metal oxides [16]) with modulated interaction with Pt-based nanoparticles has been proven to be a successful route to accelerating the MOR. Graphene, as a two-dimensional carbon material, is a one-atom-thick sheet of sp^2-bonded carbon atoms that are densely packed into a honeycomb crystal lattice. This material has attracted much attention as the catalyst support due to its unique structure, superior stability, large surface area (theoretical specific surface area: 2600 m^2 g^{-1}) and excellent electrical conductivity [17,18]. For example, Li and co-workers have prepared graphene nanosheets decorated by Pt nanoparticles, which display better catalytic activity and stability for the MOR than the conventional carbon black supported Pt (Pt/C) catalyst [19]. However, the uniform loading of Pt nanoparticles on graphene surface is difficult due to its lower level of defects and smooth surface, which deteriorates the catalytic activity of Pt nanoparticles towards the MOR. The defect level of graphene can be increased by doping heteroatoms such as nitrogen [20,21], boron [22,23], phosphorus [20] and sulfur [24], which is rather beneficial to anchoring Pt nanoparticles. More importantly, the density of electronic states of graphene can be adjusted by the heteroatom doping, which will directly influence the MOR activity and stability of Pt nanoparticles.

It has been discovered that nitrogen-doped graphene supported Pt nanoparticles (Pt/NG) exhibit higher activity and stability towards the MOR than commercial Pt/C catalyst [25]. Furthermore, the pyridinic type nitrogen in nitrogen-doped graphene has been found to be better for enhancing the catalytic activity of Pt nanoparticles towards the MOR [26,27]. The enhanced catalytic performance of Pt/NG catalyst is ascribed to the increased interaction between Pt nanoparticles and the delocalized π bond of nitrogen doped graphene by transferring electrons from Pt atoms to nitrogen doped graphene, because nitrogen has higher electronegativity than carbon and Pt [25,28]. According to the d-band center theory from Nørskov [29,30], this electron transfer shifts positively the d-band center of Pt, which increases the chemisorptions of oxygen-containing groups (OH_{ads}) and accelerates the CO oxidation by the so-called bifunctional mechanism [31]. In comparison with nitrogen, boron has lower electronegativity than carbon and platinum, and thus donates electron. Therefore, from the perspective of electronic interaction between Pt and support, boron-doped graphene (BG) as a support will have a distinctive impact on the MOR of Pt nanoparticles from nitrogen-doped graphene. However, up to now, few studies on the BG as the support of Pt catalysts for the MOR have been reported [32], and more importantly, the underlying mechanism of BG acting on the MOR activity of Pt catalysts is still unclear.

In this paper, we prepare BG by thermal-annealing of graphene oxide in the presence of boric acid, onto which Pt nanoparticles are deposited via a microwave-assisted polyol process. The influence of the BG support on the MOR activity of Pt nanoparticles and the underlying mechanism are investigated. Thus obtained Pt/BG catalyst exhibits rather high CO tolerance and thus excellent catalytic activity towards the MOR, due to the incorporation of boron atoms into the carbon networks. It is revealed that low adsorption strength of the poisoning intermediates on the Pt/BG surface, rather than the common bifunctional mechanism, as well as the uniform loading of Pt nanoparticles on boron-doped graphene, is mainly responsible for the enhanced MOR catalytic properties.

2. Experimental

2.1. Preparation

2.1.1. Graphene oxide

Graphene oxide was prepared according to the classical Hummers method [33]. In brief, 2.0 g graphite and 72 mL concentrated H_2SO_4 were stirred together for 1 h, followed by the slow addition of 24 mL concentrated HNO_3. Then, 10.0 g $KMnO_4$ was slowly added into this mixture with continuously stirring for 120 h at room temperature. After the addition of 500 mL water, excess H_2O_2 (30 wt% aqueous solution) was added and stirred for 2 h. The resulting product was filtered, washed firstly with a mixture of 35 mL HCl, 15 mL H_2O_2 and 500 mL water and finally with excess water until pH value was neutral, and obtained by freeze drying.

2.1.2. Graphene and boron-doped graphene

Boron-doped graphene was synthesized through the thermal annealing of graphene oxide in the presence of boric acid. Briefly, graphene oxide was thoroughly mixed with boric acid aqueous solution by ultrasonic agitation. This mixture was freeze-dried to remove the water. The sample obtained was placed into a quartz tube furnace followed by flowing H_2/Ar gases (H_2 5%/Ar 95%) for 30 min to remove the oxygen residues in the tube, then heating to 1000 °C at a rate of 5 °C min^{-1} and kept at this temperature for 2 h. Finally, the sample was washed with hot water to remove residual boric oxides and dried in vacuum. For comparison, graphene was prepared by heating graphene oxide under the same condition in the absence of boric acid.

2.1.3. Pt/BG catalyst

The Pt/BG catalyst with 40 wt% Pt loading was prepared by a microwave-assisted polyol process in ethylene glycol solution [34]. 20 mg boron-doped graphene was first dissolved in 10 mL isopropyl alcohol and 40 mL ethylene glycol. After ultrasonic treatment for 1 h, the mixture was magnetically stirred for 6 h at room temperature. 0.6 mL $H_2PtCl_6 \cdot 6H_2O$ solution (0.115 mol L^{-1}) was then added to the mixture and the pH value was adjusted to 11 using 1.0 mol L^{-1} NaOH solution. Argon gas was bubbled into the mixture for 30 min to remove dissolved oxygen. Subsequently, the mixture was heated in a microwave oven (2450 MHz, 800 W) for 60 s to reduce $H_2PtCl_6 \cdot 6H_2O$ into Pt nanoparticles. After cooling down to room temperature under stirring, pH value of the mixture was adjusted to 2 by adding 0.1 mol L^{-1} HNO_3 and stirred for 12 h to deposit Pt nanoparticles on the support. Finally, the Pt/BG catalyst was separated by dialysis and filtration, washed thoroughly with a large amount of ethanol and water, and dried at 80 °C in vacuum for 12 h. Graphene supported Pt nanoparticles (Pt/G) with 40 wt% Pt loading were also prepared by the same procedure, except that graphene was employed to replace boron-doped graphene.

2.2. Physical characterization

The morphology and structure of graphene, boron-doped