



# Synthesis of boron and nitrogen doped graphene supporting PtRu nanoparticles as catalysts for methanol electrooxidation



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## ABSTRACT

In this study, we demonstrate a single-step heat treatment approach to synthesize boron and nitrogen doped graphene supporting PtRu electrocatalysts for methanol electro-oxidation reaction. The reduction of graphene oxide, boron or nitrogen doping of graphene and loading of PtRu nanoparticles happened simultaneously during the reaction process. The morphologies and microstructures of the as-prepared catalysts were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The electrocatalytic methanol oxidation activity and durability of the obtained catalysts were evaluated by the cyclic voltammetry and chronoamperometric techniques. The results reveal that the boron and nitrogen doped graphene supporting PtRu electrocatalysts can be successfully prepared by the single step heat treatment technique, and the introduction of boron or nitrogen containing function groups into the reduced graphene sheets could modulate the particle size and dispersion of the supporting PtRu nanoparticles and improve the electrocatalytic performance of methanol oxidation reaction. The optimal annealing temperature is 800 °C, the preferable heat treatment time is 60 min for the nitrogen-doped catalysts and 90 min for the boron-doped catalysts, and the catalysts prepared under such conditions present superior catalytic activities for methanol oxidation than those prepared under other heat treatment conditions.

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## 1. Introduction

Direct methanol fuel cells (DMFC) are attractive power sources for various applications due to their simple structures, easily carrying, low pollution, high energy density and low operation temperature [1,2]. Currently, the key barriers to the commercial viability of DMFCs are the insufficient catalytic activity and durability, the catalyst nanoparticle growth and agglomeration, the performance degradation caused by methanol crossover and incomplete oxidation of intermediate reaction products, etc [3–6]. Pt is widely used as catalyst for both anode and cathode reactions for fuel cells, while for DMFC, the pure platinum has some specific weakness such as the relatively low electrochemical activities, easy poisoning by the formation of methanolysis carbonaceous mesophase and fast attenuation of the performance. To improve the performances and reduce the cost, a series of studies have been conducted and the PtRu alloy is found to show much better

catalytic activities than pure Pt. The excellent electrocatalytic activities and poisoning tolerance of PtRu are mainly ascribed to the synergies of the bifunctional binary alloy [7–9]. During the oxidation of methanol, the absorption and dehydrogenation of methanol are carried out on the surface of Pt atoms, accompanying with the production of CO-like intermediate species, while on the surface of Ru atoms, some oxygenic species such as OH<sup>-</sup> are absorbed and then react with the CO-like species, to eliminate the poisoning of Pt [7–9]. Since the PtRu alloy is presently the most effective catalyst for electro-oxidation of methanol in acidic media, it has been considered as the most promising anode catalysts in the DMFC. Although the structure and morphology optimizations of PtRu catalyst have been extensively conducted, its electrocatalytic activity and stability still need to be improved to meet the target for practical application [10–13].

Aside from the active metal catalyst, it is generally believed that the surface chemistry and structure of the support materials can greatly influence the performances of the resultant catalyst [13–15]. Up to date, all kinds of carbon materials, such as carbon black, carbon fiber, carbon nanotube and graphitized carbon, have been widely used as the catalysts support materials [14,16–20].

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Recently, graphene, a new and efficient catalyst support material for fuel cell electrocatalyst, has attracted great attention due to its superior electrical conductivity, high surface-to-volume ratio, ultrathin thickness, high structural flexibility and chemical stability [21–26]. Even graphene itself is an attractive potential electrocatalytic support, the doping strategy on graphene may provide further benefits. For example, the boron doping and nitrogen doping are well-known to modulate the electronic, chemical and physical properties of carbon materials, resulting in modified electronic conductivity, improved nanoparticles nucleation and growth behavior during synthesis, improved interaction of the support and catalyst, and enhanced activity of the obtained materials [27–30].

In this work, we have synthesized the boron and nitrogen doped graphene supporting PtRu nanoparticles as catalysts for methanol electrocatalytic oxidation by a single step heat treatment process. First, the precursor was prepared by mixing graphene oxide, dopants (urea or boric acid), hydrochloroplatinic acid and ruthenium trichloride. Then the precursor was calcined at a specific temperature for a period of time under argon atmosphere. During the heat-treatment process, the reduction of graphene oxide, the doping of boron and nitrogen, and the nucleation and growth of PtRu nanoparticles occurred simultaneously. We have explored the influence of the calcination temperature and time on the morphology, structure and electrocatalytic property of the doped graphene supporting PtRu nanoparticles, and found that the optimal conditions for the nitrogen-doped catalyst are 800 °C and 60 min, while for the boron-doped catalyst are 800 °C and 90 min. Both optimized catalysts demonstrate improved catalyst particle size, distribution and excellent catalytic activity and stability, which might be promising for direct methanol fuel cell applications.

## 2. Experimental

### 2.1. Synthesis of graphene oxide

Graphene oxide (GO) was synthesized by a modified Hummers method as reported previously [22,31]. Briefly, 5 g flaky graphite powder and 3.75 g NaNO<sub>3</sub> were first added into a 170 ml concentrated sulfuric acid solution (98 wt.%), and the mixture was continuously stirred for 24 h. Then 22.5 g of KMnO<sub>4</sub> was slowly added into the solution with an ice-water bath and stirred for another 120 h. After that, 500 ml of H<sub>2</sub>SO<sub>4</sub> (5 wt.%) was added to the mixture with an agitation, then 45 ml of H<sub>2</sub>O<sub>2</sub> (30 wt.%) was added and the solution was stirred for 2 h. Finally, 2 L aqueous solution containing 38 wt.% H<sub>2</sub>SO<sub>4</sub> and 1 wt.% H<sub>2</sub>O<sub>2</sub> was used to wash the suspension by a centrifuge, and then deionized water was used until reaching a neutral pH.

### 2.2. Synthesis of doped graphene supporting PtRu nanoparticles

The nitrogen-doped graphene supporting PtRu nanoparticles were prepared as follows. 16 ml of hydrochloroplatinic acid aqueous solution (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, 10 mg/ml) and 6.4 ml of ruthenium trichloride aqueous solution (RuCl<sub>3</sub>·3H<sub>2</sub>O, 10 mg/ml) were successively added into the GO suspension (48.4 ml, 5.76 mg/ml) with vigorous agitation, the molar ratio of Pt and Ru was 1.27: 1. Then 836.4 mg of urea and 480 mg of ammonia chloride were added to the solution. Subsequently, the mixture was dried at 40 °C for 24 h under continuous stirring. The obtained precursor was ground and put into a quartz tube, and then flowed with argon for 1 h to remove the air. Then the reaction system was moved into a tube furnace which was preheated to the target temperature, and kept for a desired duration. Typically, for example, one nitrogen-doped graphene supporting PtRu nanoparticle catalyst was obtained

by calcination at 800 °C for 60 min, the sample was marked as PtRu-NG-800-60, and the same nomenclature was applied for the other samples. The boron-doped and undoped graphene supporting PtRu catalysts were similarly marked as well. During the heat-treatment process, argon was kept on flowing. After the reaction, the unit was taken out of the furnace immediately and cooled down to room temperature in several minutes with a much higher argon flow. The obtained powder was ground and washed by 1 M hydrochloric acid, alcohol and plenty of deionized water, and then dried at 60 °C for 12 h in an oven. The heat-treatment conditions have been optimized by a series of control experiments with various calcination temperatures and treating durations.

The boron-doped and undoped graphene supporting PtRu catalysts were synthesized by a similar procedure to explore the influence of different dopants on the properties of methanol oxidation reaction. To prepare the boron-doped graphene supporting PtRu catalysts, boric acid was used as the boron source. First, 48.4 ml of GO suspension (5.76 mg/ml) was put into a beaker, then 16 ml of hydrochloroplatinic acid aqueous solution (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, 10 mg/ml) and 6.4 ml of ruthenium trichloride aqueous solution (RuCl<sub>3</sub>, 10 mg/ml) were added with vigorous agitation. Then 836.4 mg of boric acid was added. Similar as the nitrogen doped sample, the precursor was first dried at 40 °C for 24 h and then calcined in the tube furnace at a preset target temperature for a desired duration. As for the undoped graphene supporting PtRu catalysts, the procedure is similar except that no dopants (urea or boric acid) was added during the preparation process of the precursor.

### 2.3. Characterization

The morphologies of the catalysts were measured by a scanning electron microscopy (SEM, PHILIPS XL30TMP) with an acceleration voltage of 15 kV. X-ray powder diffraction (XRD) was carried out by using an Xpert Pro MPD diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) and the diffraction data was obtained for  $2\theta$  angles from 20° to 80°. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a VG Multilab 2000 apparatus. The microstructures and distribution of the alloy nanoparticles on graphene sheets were investigated with the transmission electron microscopy (TEM, FEI Tecnai G20) at an acceleration voltage of 200 kV.

### 2.4. Electrochemical measurements

The electrochemical performances of the samples were evaluated by cyclic voltammetry in a standard three-electrode system using CHI660D electrochemical workstation. An Ag/AgCl electrode was used as the reference electrode, all the potentials reported are vs. Ag/AgCl, and a graphite rod was used as the counter electrode. A glassy carbon electrode was used as the working electrode which was covered with the catalysts. To prepare the working electrode, 5 mg of the catalyst was first dispersed in a 250  $\mu$ L alcohol-nafion mixture ( $V_{\text{nafion}}:V_{\text{alcohol}} = 1:9$ ) by stirring. Then 5  $\mu$ L of the dispersion was dropped onto the surface of the pre-cleaned glassy carbon electrode by using a microsyringe. Finally, the electrode was dried in an oven at 60 °C for 1 h, and then cooled down in air at room temperature. The electrolytic cell was flowed by high-purity argon for at least 20 min before the electrochemical measurements. Cyclic voltammetry measurements were conducted in an electrolyte solution of 1 M CH<sub>3</sub>OH and 0.5 M H<sub>2</sub>SO<sub>4</sub> with scan rates of 10, 20, 50, 100 and 200 mV s<sup>-1</sup> between 0 and 1.0 V. Chronoamperometry tests for methanol electrooxidation were conducted in 1 M CH<sub>3</sub>OH + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at 0.6 V.

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