Simultaneous Pt deposition and nitrogen doping of graphene as efficient and durable electrocatalysts for methanol oxidation

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ABSTRACT

Nitrogen doping could effectively enhance the catalytical activity of graphene-supported Pt nano-electrocatalysts for methanol oxidation reaction. Previously, the main strategy to the synthesis of Pt/N-graphene is the two-step reaction while it involves the complicated synthesis. In this work, we describe a facile and simple one-pot reaction including the reduction of graphene oxide, nitrogen doping of graphene, and uniform deposition of Pt nanoparticles on doped graphene. Compared with the Pt/graphene catalyst without nitrogen-doping, Pt/N-graphene exhibits excellent activity and durability towards methanol oxidation reaction, which is mainly ascribed to the contribution of the improved dispersion of Pt nanoparticles and the enhanced interaction between it and nitrogen-doped graphene. It is expected that this facile, green and economic single-step synthesis approach for the Pt/N-graphene electrocatalyst could be widely utilized to the nitrogen-doped graphene catalysts.

Introduction

With the continuously increasing demand of energy along with depletion of conventional fossil fuel reserves and the rapidly escalating environmental problems, direct methanol fuel cells (DMFCs) as alternative green and sustainable power sources have aroused tremendous research interest in academic and engineering circles [1—3]. As a key component of DMFCs, Pt based catalysts are still under widespread investigation and have shown exciting performance [4]. However, to move towards their successful commercialization, focusing solely on their catalytic activity is not sufficient enough.

Instead, more effort is also required to improve their stability and to decrease costs [5].

Graphene, a monolayer of carbon atoms packed into a dense honeycomb crystal structure [6], which possesses unique nanostructure and a variety of fascinating properties has attracted considerable theoretical and experimental attentions in recent years. It has been extensively studied that graphene-based materials can be considered as promising support materials for Pt-based electrocatalysts [7]. To improve the catalytic activity of Pt nano-electrocatalyst, various methods have been applied to modify the graphene support properties [8—11], Doping carbon supports with heteroatoms such as nitrogen, boron, or sulfur has shown an effective way

to enhance the catalytic properties of Pt nanoparticles supported on carbon [12–15]. Previously, we developed a boron-doped carbon nanotube as the support materials of Pt nanoparticles, showing significantly enhanced electrocatalytic activity towards methanol oxidation [16]. Among various doping elements, nitrogen doping is most extensively investigated, which can enhance the conductivity of graphene and modify the interaction between Pt and the support [17,18]. Though there are a few studies on Pt-NG catalysts, the relatively complicated multi-step fabrication procedures have limited the large-scale catalyst synthesis [19]. Previously, the main strategy to the synthesis of Pt-NG is the two-step reaction: doping graphene with nitrogen first by the hydrothermal treatment or high-temperature annealing with N sources followed by the subsequent reduction/deposition of Pt nanoparticles [20]; or preparing graphene supported Pt nanoparticles first followed by N doping by plasma treatment [21]. The above two-step strategies make the synthesis of the electrocatalysts complicated.

In this work, we proposed an efficient "one-pot" hydrothermal method to synthesize well-dispersed electrocatalysts, Pt nanoparticles anchored on the surface of nitrogen-doped graphene (Pt-NG). As demonstrated in Fig. 1, the simultaneous reduction of graphene oxide, nitrogen doping of graphene using urea, and Pt reduction/deposition on the nitrogen doped graphene are simultaneously realized during the one-step hydrothermal process in a mixture of urea, formic acid and sodium citrate. Here, urea actes, formic acid and sodium citrate are respectively act as N doping source, reducing agent, and stabilizers. As a comparison, Pt supported on graphene without nitrogen doping (denoted as Pt-G) was also synthesized with the same method in the absence of urea. The morphology, structure characteristics, and electrocatalytic performance of the obtained two catalysts were systematically characterized and evaluated. The as-prepared Pt-NG catalysts show significantly improved electrocatalytic activity for methanol oxidation as well as enhanced stability, compared with Pt-G catalysts. The improved electrochemical performance of Pt-NG was attributed to the improved Pt dispersion, the modified electronic properties, and the strengthened interaction between Pt and nitrogen-doped graphene.

Experimental section

Synthesis of electrocatalysts

Graphene oxide (GO) was synthesized from flaky graphite powder by a modified Hummers method. In brief, 5 g of crystalline flake graphite, 2.5 g of sodium nitrate, and 120 ml of concentrated sulfuric acid were put into a round-bottom flask and stirred for 2 h at 0 °C. Then 12 g of potassium permanganate was gradually added to obtain a black-green solution which was continuously stirred for 2 h. The product was then further treated by 200 ml of ultrapure water for 0.5 h at 38 °C, followed by the addition of 38 ml of 30% hydrogen peroxide. The mixture slurry was then washed with diluted hydrochloric acid and ultrapure water until the supernatant solution obtained a pH of 7, where it was then dried in an oven at 60 °C for 24 h to obtain graphite oxide. 80 mg of graphite oxide was mixed with 60 ml of ultrapure water and then ultrasonicated for 1.5 h to create a homogeneous dispersion of graphene oxide.

The as-synthesized GO solution was mixed with 9.2 ml of chloroplatanic acid (H_2PtCl_6) (10 mg ml^{-1}), 0.1550 g of sodium citrate, 8 g of urea and ultrasonicated for 2 h. After that, 8 ml of formic acid was added. The mixture was sealed in a 100 ml Telfon-lined autoclave and maintained at 180 °C for 12 h. Then the autoclave was naturally cooled to room temperature and the reactant was fully washed with ultrapure water and ethanol to remove any impurities, the sample was dried in a vacuum oven to obtain Pt/N-graphene product. For the synthesis of Pt/graphene (without doping nitrogen), the similar procedure was followed in the absence of urea.

Characterization

X-ray powder diffraction (XRD) was carried out on a Siemens D500 diffractometer with a Cu Kα source (1.54056 Å). Diffraction data were collected for 2θ angles from 10° to 90°. The morphology and microstructure of the Pt nanoparticles on graphene were investigated transmission electron microscopy (TEM, JEM-2100F). The Raman spectra were recorded at room temperature on a Horiba HR 800 with an argon ion laser
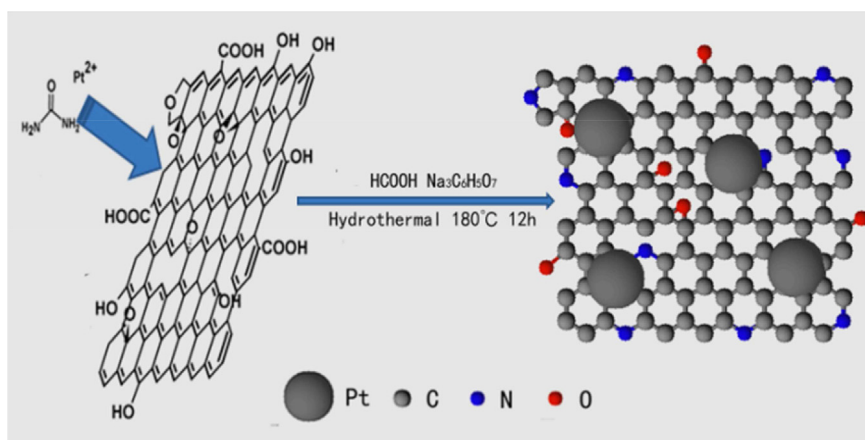

HCOOH Na₃C₆H₅O₇
Hydrothermal 180°C 12h

● Pt ○ C ● N ● O

Fig. 1 – Schematic graph of synthesis process of the Pt/N-graphene.