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Research paper

Phosphorus-doped graphene support to enhance electrocatalysis of methanol oxidation reaction on platinum nanoparticles

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ABSTRACT

Phosphorus is incorporated into graphene (PG) by thermal treating method, which is further employed as supports for Pt nanoparticles. The as-obtained Pt/PG catalyst exhibits over 2.4 times enhanced methanol electrooxidation activity compared with Pt/C, as well as desirable stability and remarkably improved CO-tolerance. These improvements are attributed to not only uniformly dispersed Pt nanoparticles that are anchored by introduced defects in PG, but also negative d-band center shift and weakened CO adsorption on Pt caused by strong interactions between Pt and PG. Consequently, PG is a promising support material for Pt-based catalysts towards methanol electrooxidation.

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1. Introduction

The direct methanol fuel cell (DMFC) is one of promising electrochemical devices, which is able to convert the chemical energy of methanol and oxygen into electric energy with high efficiency [1]. DMFC can be employed as the power source for portable electronics and electrical vehicles due to its high theoretical energy density, low-temperature operation, quick start-up, and zero SOx and NOx emission [2]. However, the sluggish kinetics of anodic methanol oxidation reaction (MOR) remarkably hinders the further development of DMFCs. To enhance the MOR kinetics, Pt and its alloys supported by carbon black materials are widely employed for MOR [3]. Recently, MOR has been revealed to be highly dependent on the features of support materials in addition to the compositions of catalytic Pt-based nanoparticles [4]. This is likely because that the strong interactions between catalytic nanoparticles and supports are pivotal for promoting the MOR kinetics and stability under harsh electrochemical environments [5–7]. In this regard, it is urgent and a hot topic to develop novel support materials, such as SnO_2 [8], TiO_2 [9] and CeO_2 [10], as alternatives for MOR electrocatalysts and enhance the strong interactions because the widely-used carbon black supports have weak interactions with Pt-based particles [11,12]. However, the low electronic conductivity of above-mentioned metal oxides is not favored for improving the electrochemical performance.

As a two-dimensional material, graphene has emerged as a promising support material because of its unique properties including large surface area, excellent stability and ultrahigh electrical conductivity [13,14]. However, the highly graphitized graphene leads to barriers for loading catalytic nanoparticles uniformly. The primary challenges are few loading sites on graphene and weak interactions between particles and graphene [15]. To address these issues, heteroatom doping is an efficient strategy to modify graphene, increasing defect site density and enhancing its interactions with catalytic particles [16]. For example, nitrogen-doped [17] and sulfur-doped graphene [18,19] were reported as promising support materials for Pt nanoparticles and presented greatly enhanced electrochemical performance. In addition to activity, the significantly increased defect sites effectively anchor Pt nanoparticles, inhibit Pt agglomeration on graphene and remarkably improve the stability [20–23]. It is notable that the electronegativities of both nitrogen (3.04) and sulfur (2.58) atoms are higher than carbon (2.55) atoms [24–26]. Therefore, it is of great interest to investigate dopants with lower electronegative in graphene supports, e.g. phosphorus (2.19) [27], which was rarely studied and reported.

Herein, phosphorus-doped graphene (PG), which is facilely prepared through annealing phosphoric acid and graphene oxide together, is employed as the support material to synthesize Pt/PG catalyst using a microwave-assisted polyols method. It is

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demonstrated that phosphorus with lower electronegativity is successfully doped into graphene matrix, which not only generates more defect sites for anchoring Pt nanoparticles, but also donates electrons to adjacent carbon atoms and further tunes the electronic structure of Pt. Thus, the Pt/PG catalyst shows outstanding catalytic performance (both activity and stability) for the MOR in acidic media. This report provides a prospective alternative method to improve the MOR performance of Pt-based catalysts for the DMFC.

2. Experiment

2.1. Material synthesis

2.1.1. Graphene and phosphorus-doped graphene

Graphene oxide (GO) was synthesized with a classic Hummers' method [28]. Briefly, 5 g of flake graphite powder was added into 180 mL of sulfuric acid solution and magnetically stirred for 1 h at 25 °C. 60 mL of nitric acid was then added into the solution. When the solution was cooled to 25 °C, 25 g of potassium permanganate was slowly added and stirred for 120 h. Subsequently, the solution was diluted with 600 mL of ultrapure water, and hydrogen peroxide (30 wt% aqueous solution) was added until the suspension turned into bright yellow. The GO sample was repeatedly cleaned and centrifuged until the solution was neutral before obtaining GO samples by frozen drying.

150 mg of GO and 160 μL of phosphoric acid were added into 150 mL of water to form a homogeneous mixture. After ultrasonicating for 3 h, this mixture was frozen dried. The resulted precursor was sintered at 800 °C for 2 h under H_2/Ar (5%/95%) atmosphere. Phosphorus-doped graphene (PG) was obtained after cooling down. For comparison, the graphene (G) without P doping was prepared by the same procedures except that no phosphoric acid was added in precursors.

2.1.2. Pt/G and Pt/PG catalysts

The microwave-assisted polyol method was used to prepare 40 wt% Pt/PG or Pt/G catalyst [29]. In brief, 10 mg of PG or G was added into the solution containing 40 mL of ethylene glycol and 10 mL of isopropyl alcohol, which was stirred for 12 h. Subsequently, 0.3 mL of 0.117 mol L^{-1} $H_2PtCl_6{\cdot}6H_2O$ solution was added into the mixture and further stirred for 1 h. The pH value of the mixture solution was adjusted to 10.5 through adding 2 mol L^{-1} NaOH solution. Then, this mixture was moved to a microwave oven and heated for 60 s under N_2 atmosphere. After cooling down, the pH value of the mixture was adjusted to below 2 by using 2 mol L^{-1} HNO_3 solution followed by another 24 h stirring. The Pt/PG or Pt/G catalysts were obtained by dialysis and drying at 70 °C for 3 h.

2.2. Physical characterization

The transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images were obtained form a Hitachi H-7650 equipment with an acceleration voltage of 200 kV. The inductively coupled plasma mass spectrometry (ICP-MS) was used to detect the platinum content of Pt/G and Pt/PG catalysts on Vista MPX equipment. Raman spectroscopy was measured on a Thermo Nicolet Dispersive XR Raman Microscope with an excitation wavelength of 457.9 nm. XRD patterns were obtained on a Rigaku TTR-III X-ray diffractometer with Cu Kα radiation (λ = 0.1506 Å). XPS was conducted on a ThermoFisher-VG Scientific (ESCALAB 250Xi) photoelectron spectrometer using monochromic Al X-ray radiation (1486.6 eV).

2.3. Electrochemical tests

All electrochemical measurements were conducted on a conventional three-electrode cell using a CH Instrument 604D electrochemical workstation at the room temperature. Catalyst films on

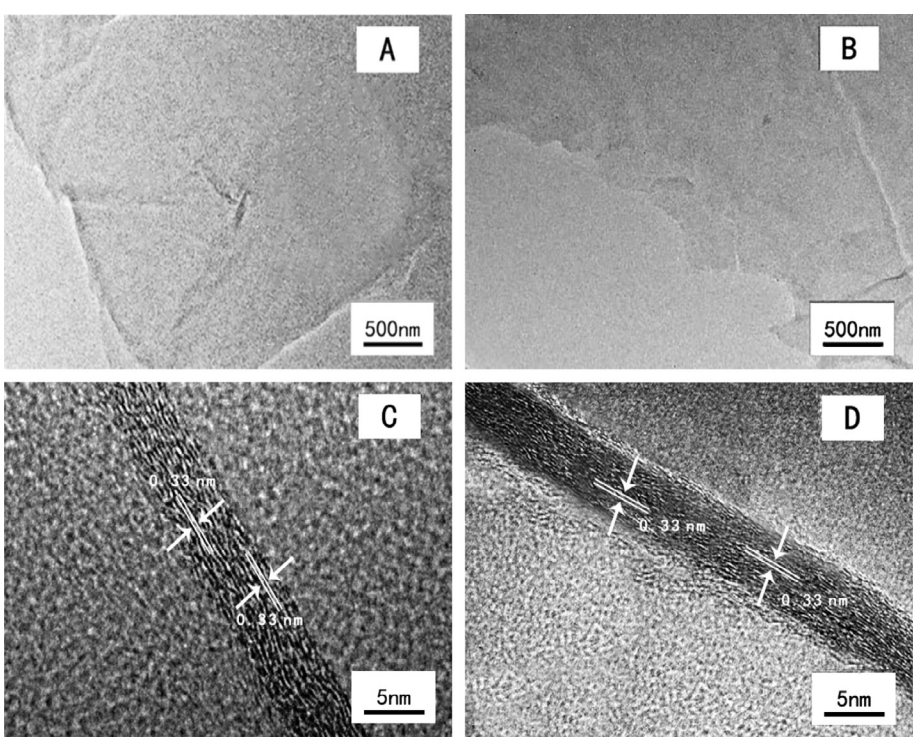

Fig. 1. TEM and HRTEM images of G (A, C) and PG (B, D).

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