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Facile synthesis of boron and nitrogen-dual-doped graphene sheets anchored platinum nanoparticles for oxygen reduction reaction

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ABSTRACT

Boron and nitrogen-dual-doped graphene sheets (BNG) has been conveniently synthesized by a novel strategy, including one-step pyrolysis of nitrogen and boron-containing borane-tert-butylamine complex impregnated with cobalt ions. The BNG with a relatively high boron and nitrogen-doping level is used it as Pt support for oxygen reduction reaction for the first time. An excellent electron-donating of BNG to Pt that facilitates the reduction of O_2 and strengthens BNG/Pt interaction has been evidenced. The novel Pt/BNG catalyst exhibits highly improved electrocatalytic activity and stability compared with commercial Pt/C. In O_2-saturated 0.1 M $HClO_4$, the Pt/BNG catalyst shows a mass activity of 213.6 mA mg^{-1}_{Pt} at 0.9 V *vs.* RHE, which is nearly three times as high as that of commercial Pt/C. In addition, the Pt/BNG catalyst displays much higher stability than Pt/C in continuous potential cycling tests.

1. Introduction

The proton exchange membrane fuel cell (PEMFC) is considered to be one of the most promising energy conversion devices for portable electronic devices and electric vehicles because of its relatively low operating temperature, environmental friendliness and high energy conversion efficiency [1,2]. But its large-scale commercialization is hindered by the high overpotentials and slow kinetics of current catalysts for oxygen reduction reaction (ORR) at the cathode [3–5]. Until now, platinum (Pt)-based catalysts are still considered as the most efficient electrocatalysts for ORR and considerable attention has been paid during the past decades [6–8]. Although fruitful developments has been achieved, the high cost, unsatisfactory stability and scarcity of Pt still hinders the successful commercialization of PEMFCs and compelled scientists to reduce the amount of Pt usage [9,10]. Therefore, improving electrocatalytic activity and stability of Pt to reduce the amount of Pt usage is still required and is a critical challenge.

Finding proper supports that can promote electrocatalytic activity and stability of Pt is an effective method for reducing Pt usage [11,12]. Graphene, one of the most attractive carbon nanostructures, exhibits intriguing potential benefits as electrocatalyst supports in fuel cells for its high surface area, good electrical conductivity, strong mechanical strength and high chemical stability [13,14]. Nevertheless, pure graphene is not always the most suitable candidate for electrocatalyst support due to its low inherent catalytic activity and relatively inert surface. Substitutional doping of graphene with heteroatoms (N, B, P and S) can significantly tailor the electronic structure and catalytic properties of graphene. Very recently, Pt supported on heteroatom-doped graphene has demonstrated superior electrocatalytic activity and stability for both methanol oxidation and oxygen reduction [15–17].

Herein, we developed a facile synthesis of boron and nitrogen-dual-doped graphene sheets (BNG) by a single-step pyrolysis of a boron and nitrogen-containing borane-tert-butylamine complex impregnated with cobalt ions. Compared with single-doping carbon, co-doping carbon with boron and nitrogen can effectively create more catalytically active sites because of synergistic coupling effects of these two elements [18–20]. Both electron-rich nitrogen and electron-deficient boron dopants are inclined to break the electroneutrality of sp^2 carbon and reduces the chemisorption overpotential of O_2, resulting in highly efficient ORR catalytic activity [21,22]. Therefore, the BNG with inherent ORR electrocatalytic

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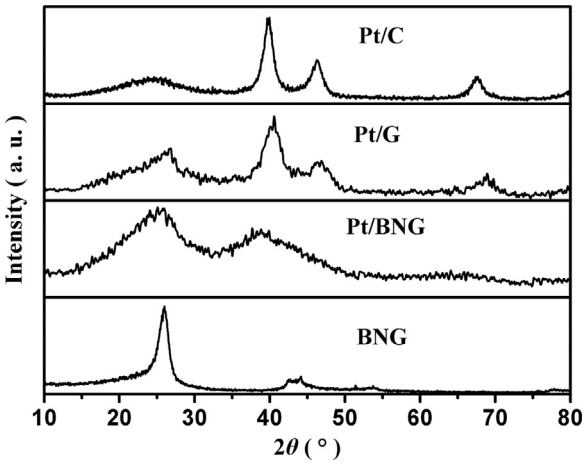

Fig. 1. XRD patterns of the as-synthesized BNG, Pt/BNG, Pt/G and commercial Pt/C catalysts.

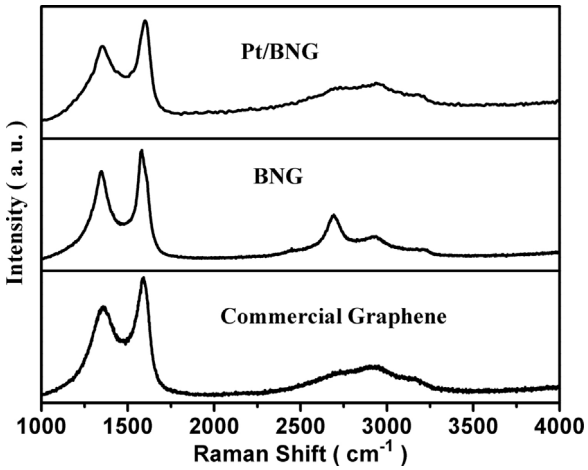

Fig. 2. Raman spectra of commercial graphene, as-synthesized BNG and Pt/BNG.

activity is favorable to synergistically enhances performance toward ORR when used as Pt support. In addition, boron and nitrogen dual-doping graphene sheets with defects can facilitate uniform dispersion of Pt nanoparticles and strengthen interaction between BNG and nanoparticles. As a result, the Pt/BNG catalyst shows much highly enhanced electrocatalytic activity and stability for ORR.

2. Experimental

2.1. Synthesis of BNG and Pt/BNG

Boron and nitrogen-dual-doped graphene sheets (BNG) was prepared by pyrolysis of a borane-tert-butylamine complex impregnated with cobalt ions. After dissolving cobaltous chloride hexahydrate (0.02 mol, Kemiou Chemical Reagent Co., Ltd.) in

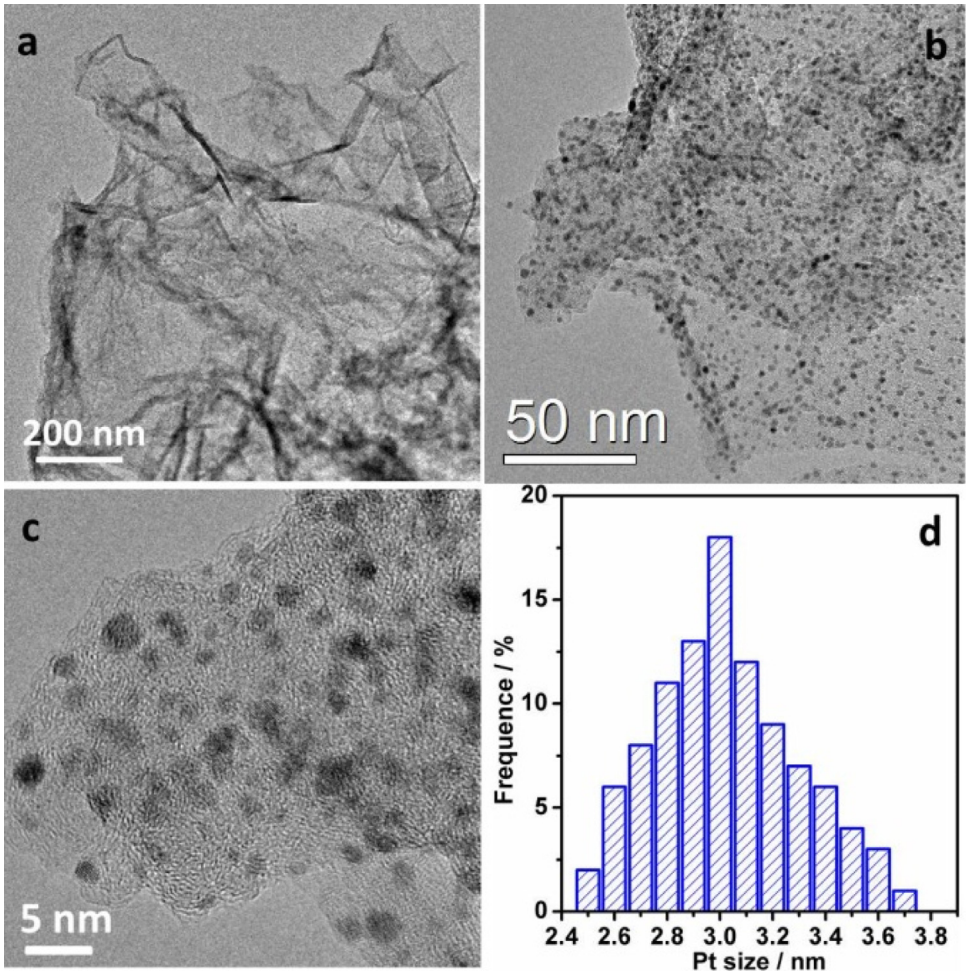

Fig. 3. (a-c) TEM and HRTEM images of the Pt/BNG and (d) size-distribution histogram of the Pt nanoparticles on the Pt/BNG.