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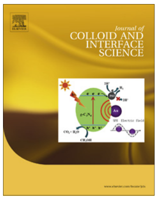

Superior catalytic performances of platinum nanoparticles loaded nitrogen-doped graphene toward methanol oxidation and hydrogen evolution reaction

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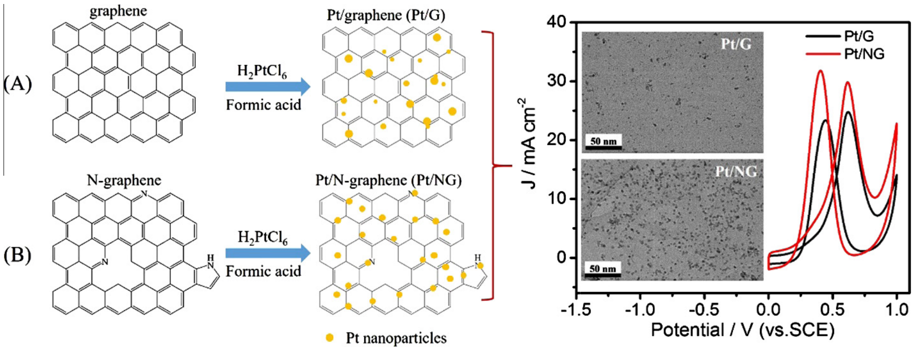
GRAPHICAL ABSTRACT

The Pt nanoparticles loaded nitrogen-doped graphene (Pt/NG) was efficiently prepared by employing formic acid as the reduction agent free of any surfactant or hydrothermal process. The resultant Pt/NG exhibited superior catalytic activity toward methanol oxidation and hydrogen evolution reaction, which was ascribed to the high Pt loading and nitrogen doping.



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ABSTRACT

The catalysts with excellent catalytic properties and low-cost are still highly desirable in many fields, such as fuel cells. In respect of this challenge, we have synthesized high-quality platinum nanoparticles loaded nitrogen-doped graphene (Pt/NG) by using formic acid as reduction agent and commercial-available nitrogen-doped graphene (N-graphene) as supporting materials. The morphology and component characterization demonstrate that high-loading Pt nanoparticles with a mean diameter of 2.5 nm were uniformly dispersed on nitrogen-doped graphene. The resulting Pt/NG exhibit higher catalytic activity toward methanol oxidation and hydrogen evolution reaction compared with commercial Pt/C or self-synthesized platinum nanoparticles-loaded graphene. The superior catalytic performance of Pt/NG are discussed, and ascribed to the well-dispersed Pt nanoparticles and abundant edge plane sites on N-graphene. The resultant Pt/NG with high catalytic properties and cost-effective may emerge as a promising high-performance catalyst for fuel cells.

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1. Introduction

Platinum based materials have been widely investigated for the excellent catalytic activity for numbers of reactions, such as oxidation of fuel molecules (methanol, ethanol) [1,2], oxygen reduction reaction (ORR) [3], and hydrogen reduction reaction (HER) [4], which are of vital importance in fuel cells. However, the large-scale applications have seriously hindered by the high-cost and limited reserve of Pt [5]. Thus, extensively efforts have been devoted to the improvement of efficient utilization of Pt in these catalytic processes [6].

To achieve the high utilization of Pt, carbon materials with abundant edge-plane sites, high surface area as well as superior conductivity are proved to be the ideal supports for catalysts [7]. Recent years, graphene has emerged as high-performance supporting materials for a serious of catalysts due to the tunable surface chemistry, high chemical stability and relatively low-cost [8]. For instance, FePt nanoparticles loaded graphene composite (FePt/graphene) has been reported to display superior catalytic activity and stability toward ORR that the FePt/graphene retains its high activity even after 10,000 potential sweeps [9]. Heteroatom, such as nitrogen and sulfur doped carbon nanomaterials have shown enhanced activity toward ORR and HER derived from the modulation of electrical structure and improvement of conductivity due to the presence of heteroatom in the graphene lattice [10,11]. Meanwhile, the substitutional doping of heteroatom could introduce more defect sites into the graphene plane which could facilitate the anchor of nanoparticles [12,13]. Previous reports have demonstrated that nitrogen doped graphene (N-graphene) is the suitable supporting material for Pt NPs due to the unique properties of pyridinic type nitrogen [14]. Solvothermal approaches using ethylene glycol as the reducing agent are frequently employed for the anchoring of Pt nanoparticles on carbons [15]; however, these methods require solvothermal process and relatively complex sample handling.

In response, we prepared the Pt nanoparticles-loaded N-graphene (Pt/NG) by a simple method using formic acid as reduction agent under the room temperature. The morphology and composition of Pt/NG are investigated in details. The Pt nanoparticles displays a uniform dispersion on the N-graphene. The resultant Pt/NG exhibits enhanced catalytic activity and durability toward methanol oxidation and hydrogen evolution reaction in comparison with Pt nanoparticles-loaded graphene and commercial Pt/C.

2. Experiments

2.1. Materials

The graphene oxide was prepared by the modified Hummers methods. The nitrogen-doped graphene with a nitrogen content of 3–5 wt.% was purchased from the Nanjing XFNANO Materials Tech Co., Ltd (Nanjing, China). The chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$, Pt $\geqslant$ 37.5%) was purchased from Aladdin Chemistry Co., Ltd (Shanghai, China). The formic acid ($\geqslant$98%) and methanol ($\geqslant$99.7%) were purchased from the Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The platinum on carbon (Pt/C, 10%) was purchased from Sigma-Aldrich.

2.2. Preparation of samples

For the preparation of Pt nanoparticles loaded N-graphene, 4 mL 0.1 mg mL^{-1} N-graphene dispersion solution was mixed with 50 μL 0.04 mol L^{-1} H_2PtCl_6 solution. After gently stirred for 0.5 h, 0.4 mL formic acid was added into the mixture solution. The solution was stirred at the room temperature for 12 h. Then, the Pt/NG was centrifuged and re-dispersed in ethanol with a concentration of 1 mg mL^{-1}. The Pt/graphene could be obtained the similar procedure.

2.3. Characterization

The morphologies of the samples were characterized by the field-emission scanning electron microscopy (FESEM, Hitachi S-4800) and transmission electron microscopy (TEM, JOEL JEM-2100). The X-ray photoelectron spectroscopy (XPS) experiments were performed on a Thermo Fisher ESCALAB 250 instrument. The Raman spectra were obtained on a Renishaw inVia Reflex spectrometer.

2.4. Electrochemical experiments

For the modification of electrodes, 3 μL 1 mg mL^{-1} sample dispersion solution was dropped on a 3 mm glassy carbon electrode, and 2 μL 0.5 wt.% Nafion solution was used to improve the stability of modified electrode. The electrochemical experiments were carried out on a CHI 660E workstation (Shanghai CH Instruments Co., China). The Zahner IM6 electrochemical workstation (ZAHNER-Elektrik Gmbh & Co., Germany) was employed for the electrochemical impedance spectroscopy (EIS) experiments in the frequency range from 10^{-1} Hz to 10^6 Hz with an applied amplitude of 5 mV.

3. Results and discussions

The Pt nanoparticles-loaded N-graphene (Pt/NG) was efficiently prepared by using formic acid as the reduction agent without any surfactant or hydrothermal process (Scheme 1). This approach takes the advantage of high hydrophilicity of N-graphene to avoid the complex process for the surface activation which are essential for the pristine carbons. Meanwhile, the abundant active edge sites on the surface of N-doped graphene, generated by the presence of nitrogen heteroatom, could benefit the nucleation and growth of Pt nanoparticles. Noteworthy, the reluctant Pt/NG are free of impurities, such as the surfactants and reduction agents which may depress the catalytic performance of catalysts [16]. As the control experiment, Pt nanoparticles-loaded graphene (Pt/G) was constructed via the same process.

The TEM and FESEM measurements are carried out to characterize the loading and morphology of the samples (Figs. 1and 1S). The characteristic wrinkles in graphene materials could be observed in the SEM images of Pt/G and Pt/NG; meanwhile, the 3-demension structure of Pt/NG may enhance the utilization of Pt NPs (Fig. S1A and 1B) [17]. For Pt/G, Pt nanoparticles show an average diameter of 1.2 nm with a relatively wide size distribution and even distinguished agglomeration (Fig. 1A); in contrast, well-dispersed Pt nanoparticles with uniform morphology are observed on N-graphene for Pt/NG, providing an average particle size of 2.5 nm (Fig. 1B). Besides, the mapping images of Pt/NG also confirm the high dispersion of Pt nanoparticles (Fig. S2). According to previous reports, the presence of nitrogen species in carbons, providing positively charged surface as well as abundant edge plane sites, contributes to the uniform dispersion and anchoring of Pt nanoparticles as well as enhances the interaction between carbons surface and nanoparticles [18,19]. For commercial Pt/C, Pt nanoparticles display relatively poor dispersion and uniformity as shown in Fig. 1C.

Generally, the intensity ratio of D-band and G-band from Raman spectra could evaluate the number of edge plane sites in carbon nanomaterials. Then, more abundant defect sites on N-graphene are confirmed by the Raman spectra results, providing