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Preparation and electrochemical characterization of nitrogen doped graphene by microwave as supporting materials for fuel cell catalysts

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ABSTRACT

A quick and efficient approach to prepare nitrogen doped graphene (NG) is proposed in this paper via microwave heating in NH_3 atmosphere. Results show that graphene, as an allotrope of carbon, is a good microwave-absorbing material and can reach a high temperature in minutes, facilitating nitrogen incorporation into the structure under NH_3. Elemental analysis and X-ray photoelectron spectroscope (XPS) verified the success of N-doping with the nitrogen content of 5.04 wt%. For comparison, both plain grapheme (G) and the NG were used as supporting materials for platinum to investigate their potential application in fuel cells. Transmission electron microscope (TEM) images showed that the NG improved the distribution of Pt particles. Themogravimetry (TG) and differential scanning calorimeters (DSC) revealed better thermal stability of the Pt/NG than that of the Pt/G. Furthermore, the Pt/NG catalysts exhibited higher electrochemical active surface area, methanol catalytic activity, and tolerance to CO poisoning than those of the Pt/G under fuel cell conditions. It suggests that the NG prepared by microwave synthesis has provided a new way to improve electrocatalytic activity in fuel cells.

1. Introduction

Since graphene was first discovered in 2004 [1,2], it has attracted great interest from both experimental and theoretical scientific communities [3]. Graphene, with a two-dimensional array of sp^2-bonded carbon atoms, exhibits high surface areas (theoretical specific surface area of $2620\,m^2\,g^{-1}$), superior electrical and thermal conductivities, excellent mechanical strength and elasticity, and ease of modification [4]. Due to the unique physical and chemical properties, graphene provides an ideal base for electronics, sensors, composites, batteries, supercapacitors and hydrogen storage [5,6].

Many efforts, such as chemical doping, have been made to further modulate the properties of graphene over past several years. Devising chemical doping method for this two dimensional material is key to its widespread potential applications [7–12]. In particular, the doping of nitrogen into carbon structures has received great attention. For graphene sheets, N-doping can enhance the electrical and thermal conductivities, and is also a leading potential strategy to enrich free charge-carrier density [6,13,14]. More importantly, the incorporation of nitrogen functional groups into carbon network can serve as active sites for anchoring metal particles, strengthening the metal-graphene interaction [15]. Several approaches have been successfully demonstrated to dope nitrogen into graphene sheets, such as joule annealing in NH_3 [16], nitrogen plasma [17], chemical vapor deposition [12,18], arc-discharge of carbon electrode [19], hydrothermal reduction in the presence of hydrazine and ammonia [20], and surprisingly by hydrazine sonication [21]. However, convenient and effective doping of graphene is still needed.

In this study, graphene (G) was first synthesized by microwave exfoliation of graphitic oxide, and N-doped graphene (NG) was then prepared by microwave-heating of the graphene in NH_3 atmosphere. It was demonstrated that graphene can absorb microwave easily and reach a very high temperature in few seconds, quickly incorporating nitrogen atoms. The N-doping method through microwave in NH_3 was efficient and fast with a high nitrogen content. Moreover, the Pt/G and Pt/NG catalysts were prepared by microwave-assisted polyol to investigate their application in half-cell reaction of direct methanol fuel cells (DMFCs). Compared to the Pt/G catalysts, Pt/NG catalysts showed better thermal stability

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and exhibited excellent performance under fuel cell operation. It suggests that the NG is a promising supporting material for noble metal catalysts in DMFCs.

2. Experimental

2.1. Preparation of G and NG

The graphitic oxide (GO) was synthesized from natural graphite powder by a modification of Hummers and Offeman's method [22,23]. Graphene was prepared by microwave-thermal expansion using GO as precursor. GO was put into a three-neck flask purged with N_2 at a rate of 100 ml min^{-1} for 5 min through a mass flow controller. Next, the flask was placed in a household microwave oven (Galanz, 2450 MHz, 700 W) under high power for 60 s to obtain graphene via the microwave-thermal expansion procedure [24–26]. To prepare the NG, the flask with graphene was purged with NH_3 at a rate of 200 ml min^{-1} for 5 min and then treated by microwave. Graphene can absorb microwave easily thus reaching a very high temperature (beyond 500 °C) in a short time. The power was on for 60 s/off for 120 s and repeated for 4 times with the flow of NH_3 at 200 ml min^{-1} in the whole process.

2.2. Preparation of Pt/G and Pt/NG composites

The Pt/G and Pt/NG catalysts were synthesized by microwave-assisted polyol process. The NG with a weight of 80 mg was dispersed in 30 ml ethylene glycol by sonication for 30 min. Then, 2.7 ml of H_2PtCl_6 solution (20 mg $H_2PtCl_6 \cdot 6H_2O$ ml^{-1}) was slowly added and the pH value of this mixture was adjusted to 12 using 1 M NaOH. The solution was placed in the microwave oven and intermittently heated in the pattern of 10 s on and 20 s off for 10 times. Next, the pH value of the solution was adjusted to 3 using 1 M HCl and subsided for 3 h. The final solution was filtered and further washed with hot water. The residue was re-dispersed in water by sonication and dried by freezing drying, which can prevent irreversible aggregation of graphene during the drying process [4]. Pt/G catalysts were synthesized by the same method for comparison.

2.3. Physical and electrochemical characterizations

The morphology of Pt nanoparticles on different carbon supports was explored by transmission electron microscope (TEM) on a JEM-200CX at 200 kV. X-ray diffraction (XRD) was conducted on a Rigaku D/MAX-Ultima III X-ray diffractometer using Cu Kα radiation (λ = 0.15406 nm). The 2θ angular range from 10° to 80° was explored at a scan rate of 10° min^{-1}. The X-ray photoelectron spectroscopy (XPS) was performed by ESCALAB 250 apparatus, using monochromated Al Kα radiation at 150 W, in the pass energy (PE) mode (PE = 20 eV). The pressure of the spectrometer was 5×10^{-10} mbar and 5×10^{-9} mbar during the measurements. Specific surface area collected on a Micromeritics Tristar-3000 surface area by using the Brunauer–Emmett–Teller (BET) model after the samples had been degassed in a flow of N_2 for 3 h. Elemental analysis was conducted on a Elementar Vario MICRO at 980 °C and 1174 mbar. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed on a STA 449C thermogravimetric analyzer from room temperature to 800 °C at a rate of 10 °C min^{-1} under air flow.

Table 1
Elemental analysis of G and NG.

Samples	C (wt. %)	H (wt. %)	O (wt. %)	N (wt. %)	C/O (at. %)
G	82.72	1.57	15.71	–	7.02
NG	82.64	2.08	10.25	5.04	10.75

Electrochemical measurements were performed at an electrochemical station (PARSTAT 2273, Princeton Applied Research). Pt foil and a saturated calomel electrode (SCE) were served as a counter electrode and reference electrode, respectively. A glassy carbon disk with a diameter of 5 mm was employed as working electrode. About 10 μg Pt of the catalyst was deposited onto the glassy carbon disk with an area of 0.196 cm^2, corresponding to Pt loading of 51.02 μg cm^{-2}. For cyclic voltammetry (CV) measurements, the working electrode was immersed in 0.5 M H_2SO_4 and 0.5 M CH_3OH solution saturated by high purified nitrogen with the potential between −0.241 and 1.0 V versus SCE. In the CO stripping experiment, the pre-adsorption of CO was achieved by bubbling CO into the solution and holding the potential at −0.15 versus SCE for 20 min. After that, the solution was purged with N_2 gas for another 20 min at −0.15 V to remove the dissolved CO in the solution. All potentials were measured and quoted against the SCE. Durability investigation of catalysts was carried out by accelerated durability test (ADT) method. ADT was conducted by potential cycling between 0.6 V and 1.2 V (NHE) at 50 mV s^{-1} in N_2 saturated 0.5 M H_2SO_4.

3. Results and discussion

Microwave treatment of the graphene under NH_3 atmosphere resulted in N doping in the G sheets. Most of the oxygenated groups in the NG were removed during the treatment [27]. Table 1 listed the elemental analysis of G and NG. Upon N-doping, the nitrogen content of NG was 5.04 wt%, while the oxygen content decreased to 10.25 wt% with the C:O atom ratio of 10.75. The results verified that the oxygen-containing functional groups were removed during the N-doping process.

XPS analysis (Fig. 1) further revealed that the surface compositions of the NG. Only carbon, oxygen and nitrogen were detected, and the content of N was slightly lower than that showed

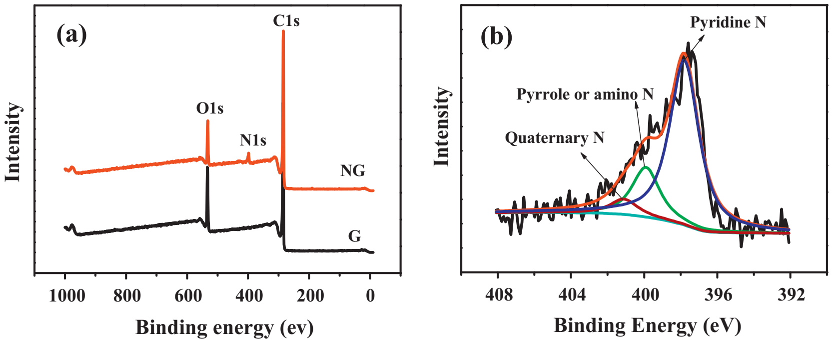

Fig. 1. The XPS survey spectra of G and NG (a) and N(1s) XPS spectra of NG (b).