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Preparation of nitrogen-doped graphene by high-gravity technology and its application in oxygen reduction

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ABSTRACT

Electrochemical oxygen reduction is key to many clean and sustainable energy technologies, including proton exchange membrane fuel cells and metal–air batteries. However, the high activation barriers in the oxygen reduction reaction often make it the bottleneck of energy conversion processes; thus, high-performance oxygen reduction electrocatalysts are desired. At present, the best commercially available oxygen reduction catalyst is based on the precious metal Pt. However, it suffers from resource scarcity and unsatisfactory operational stability, hindering its widespread and large-scale application in clean and sustainable technologies. Nitrogen-doped graphene has excellent electrocatalytic properties for oxygen reduction. In this paper, a scalable method to prepare nitrogen-doped graphene with high quality was introduced, in which the graphene oxide prepared by high-gravity technology and urea was reacted under hydrothermal conditions. Accompanying the hydrothermal reaction, graphene oxide reduction and nitrogen doping were accomplished at the same time. The effect of the content of nitrogen on the performance of nitrogen-doped graphene was investigated. When the mass ratio (graphene oxide/urea) was 1:400, the nitrogen-doped graphene had the best oxygen reduction performance. Compared with the undoped samples, the initial reduction voltage of the nitrogen-doped samples distinctly shifted 45 mV to the right. When the voltage was −1.0 V, the electron transfer number was 4.1, indicating good oxygen reduction activity. The preparation method is feasible, simple, and can be easily scaled up.

Introduction

Graphene is a two-dimensional ideal structural material with a large specific surface area (Stankovich et al., 2006). Each carbon atom employs an sp^2 hybrid orbital to form σ bonds with three adjacent carbon atoms, and each carbon atom contributes non-bonding electrons (Geim & Macdonald, 2007). Thus, the π electron orbit formed in a direction perpendicular to the plane causes graphene to have good electron transport properties, which is an important factor in the use of graphene for energy conversion and storage (Choi et al., 2012; Ferrari et al., 2015; Qu, Liu, Baek, & Dai, 2010; Yoo et al., 2008), medicine (Feng & Liu, 2011), electrocatalysis (Li et al., 2012), sensors (Arsat et al., 2009), and electronics (Dean et al., 2010). Current methods for preparing graphene include mechanical exfoliation (Blake et al., 2007), SiC decomposition (Berger et al., 2006), chemical vapor deposition (CVD) (Cui, Ruitao, & Kang, 2010), graphite intercalation (Viculis, Mack, Mayer, Hahn, & Kaner, 2005), thermal reduction (Zhang et al., 2011), and the redox method (Hummers & Offeman, 1958). Each method has its advantages and disadvantages. For example, mechanical exfoliation has a low yield, and graphene films prepared from CVD are difficult to transfer from the substrate. The oxidation–reduction method is the most promising low-cost method for the mass production of graphene. The as-prepared graphene oxide (GO), chemically functionalized with groups such as hydroxyls, carboxyls, or epoxides, is soluble in polar solvents, which is a benefit for processing. Ultrasonic exfoliation, which is always used in the oxidation–reduction method, is not easily scaled up and can create defects and uneven size distribution. To improve the quality of graphene prepared by the redox method, high-gravity technology is applied in the course of oxidation–reduction to exfoliate graphite oxide in this paper.

A rotating packed bed (RPB) with a centrifugal force of up to several hundred gravitational values can enhance the processes of mass transfer, heat transfer, and micro-mixing (Zhao, Shao, & Chen, 2010). It can significantly improve the conversion and selectivity of

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the reaction, reduce reactor volume, simplify processes, and reduce polluting emissions. In a RPB, the fluids going through the packing are spread or split into very fine droplets, threads, and thin film under the high shear field. At present, high-gravity technology is commonly applied to intensify reactions and separations. Our team used it to exfoliate graphite oxide during the preparation of GO. Compared with the ultrasound method, GO prepared by high-gravity technology had a larger surface area and fewer layers and defects (Shen, Gao, Zhao, Wu, & Yin, 2016).

The electrochemical oxygen reduction reaction (ORR) is key to many clean and sustainable energy technologies, including proton exchange membrane fuel cells and metal–air batteries. For fuel cells, the reduction path of O_2 is affected by factors such as the acidity and alkalinity of the electrolyte and electrode materials. Generally, there are three routes, including two-electron reduction, four-electron reduction, or a mixture of both. Direct four-electron reduction paths are ideal. In an acidic electrolyte environment, O_2 will be reduced to generate water. In an alkaline electrolytic environment, O_2 will obtain four electrons to become OH^-. The relative equations are as follows: $O_2 + 4e^- + 4H^+ = 2H_2O$; $O_2 + 4e^- + 2H_2O = 4OH-$. The reversibility of the ORR in the cathode is poor. Although platinum has a high catalytic activity and is the best choice for a cathode catalyst (Gasteiger, Kocha, Sompalli, & Wagner, 2005), it is a non-renewable resource with minimal reserves and is very expensive. At the same time, platinum catalysts can be poisoned by carbon monoxide produced in the fuel cell reaction (Kardash, Huang, & Korzeniewski, 2000). Therefore, to achieve long-term fuel cell development and industrialization, it is important to find new non-precious metal catalysts that can replace precious platinum. Many new cathode catalysts for fuel cells have been explored, such as non-precious metals and carbon materials. Matter, Wang, Arias, Biddinger, and Ozkan (2006) prepared nitrogen-doped CNTs by pyrolysis of acetonitrile on the surface of iron particle catalysts, and they were found to have good ORR catalytic activity. Luo et al. (2011) proposed that the electronegativity of the nitrogen atom is larger than that of the carbon atom. When the nitrogen atom is introduced into the carbon atom structure, the adjacent carbon atom will be positively charged, which is favorable to the adsorption of oxygen. Therefore, the doping of nitrogen may improve the catalytic activity of graphene. Geng et al. (2011) showed that nitrogen-doped graphene in an alkaline electrolyte solution had a good oxygen reduction activity. At present, the methods to realize graphene nitrogen doping include chemical vapor deposition (Jeong et al., 2011; Meyer et al., 2011; Qu et al., 2010; Wei et al., 2009), N_2 plasma treatment (Wang, Shao, Maston, Li, & Lin, 2010), arc discharge (Li et al., 2010; Panchakarla et al., 2009), high energy heating (Wang, Li et al., 2009), and the template method (Guo et al., 2010). Because of its simple operation and low cost, the hydrothermal method is widely studied to synthesize nitrogen-doped graphene (Hasan, Tsekoura, Sternhagen, & Strømme, 2012; Long et al., 2010; Sun et al., 2012; Zhang, Fugane, Mori, Niu, & Ye, 2012). Nitrogen sources for preparing nitrogen-doped graphene reported in the literature include ammonia gas (Jeong et al., 2011; Meyer et al., 2011; Qu et al., 2010; Wei et al., 2009), pyridine (Panchakarla et al., 2009), acetonitrile (Qian, Cui, Hao, Hou, & Zhang, 2011; Reddy et al., 2010), melamine (Sheng et al., 2011), and urea (Mou et al., 2011). Because of its high nitrogen content, solubility in water, low toxicity, ease of handling, environmental friendliness, and good reduction ability, urea is considered to be the best nitrogen source for the preparation of nitrogen-doped graphene. In this paper, nitrogen-doped graphene (NG) was prepared from GO obtained in a RPB and urea under hydrothermal conditions. The ORR properties of NG were tested, demonstrating that GO prepared in a RPB can be doped with more nitrogen. The GO has larger surface with oxygen-containing functional groups exposed than the ultrasonic.

Experimental

Materials

Graphite flakes were supplied by Nanjing Xianfeng (Nanjing, China). Sodium nitrate was purchased from Xilong Chemical Co., Ltd. (Beijing, China). Sulfuric acid (98%), potassium permanganate, hydrogen peroxide, hydrochloric acid, urea, isopropyl alcohol, and potassium hydroxide were purchased from Beijing Chemical Factory (Beijing, China). Alumina polishing powder was obtained from Tianjin Aida Hengsheng Co., Ltd (Tianjin, China). High-purity oxygen came from Xianghe Nitrogen Plant (Xianghe, China). Nafion solution (5%) was purchased from Shanghai Hesen Electric Appliance Co. (Shanghai, China).

Preparation of graphite oxide

Graphite oxide was obtained from flake graphite by a modified Hummer method (Wang, Shen, Wang, Yao, & Park, 2009). A total of 5 g of flake graphite, 2.5 g of sodium nitrate, and 120 mL of H_2SO_4 were placed in a 1000-mL beaker. Under an ice water bath and with magnetic stirring, 15 g of potassium permanganate was slowly added and stirred for 2 h. Then, the mixture was mixed for 2 h at 35 °C in an oil bath. The beaker was then transferred to an ice water bath, and 200 mL of deionized water was added. The mixture was reacted for 1.5 h under an oil bath at 98 °C. Deionized water was poured into the mixture until the volume reached 1000 mL, followed by adding 20 mL of hydrogen peroxide solution. The beaker was then sealed with plastic wrap and left for 12 h. The graphite oxide was washed repeatedly with HCl (0.1 mol/L) and deionized water until the pH approached 7.

Preparation of graphene oxide

A total of 500 mL of 1.5 g/L graphite oxide solution was pumped into the liquid–liquid rotating packed bed with a speed of 1000 rpm and filler loading rate of 40%, returned to the beaker vessel through the outlet, then re-pumped into the rotating packed bed under the action of a peristaltic pump. This exfoliation operation was repeated until the time reached 150 min. The process flow diagram is shown in Fig. 1. The inner and outer rotor diameters are 30 and 90 mm, respectively. The axial thickness of the filler is 25 mm, and the diameter of the feed tube is 8 mm.

During the exfoliating process, the suspension quickly goes through the mesh packing in the shape of a thin film laminar flow on the surface of the packing and numerous small droplets in the packing space because of the intense centrifugal force and shear force under high rotator speed. The thickness of the liquid thin film and the size of droplets can be either micrometers or nanometers. When graphite oxide moves with the liquid, it primarily suffers from two forces on its surface: shear force and collision force. The shear force, produced by a velocity gradient and parallel to the surface of graphite oxide sheets, can overcome the weak van der Waals force attraction between sheets and produce mono-layer or few-layer GO from bulk sheets. The collision effect favors an efficient fragmentation and exfoliation of graphite oxide flakes. Compared with ultrasonication exfoliation, this method possesses an obvious advantage: the rotating packed bed provides a homogeneous force field for exfoliating GO sheets.

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