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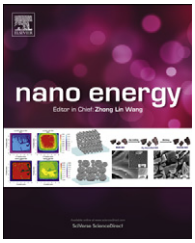

RAPID COMMUNICATION

Synthesis of amino-functionalized graphene as metal-free catalyst and exploration of the roles of various nitrogen states in oxygen reduction reaction

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Abstract
Nitrogen-containing graphene is a promising candidate for oxygen reduction reaction (ORR) in fuel cells. However, there are still some challenges in further application and modification of N-graphene and in understanding the roles of various nitrogen states on electrocatalysis. Herein, we design a simple and effective solvothermal method to synthesize amino-functionalized graphene (AG) from graphite oxide (GO) only in the presence of ammonia solution. Having a significant amount of amino species with the total nitrogen content of up to 10.6% (atom%), the resultant product can act as an efficient metal-free catalyst, exhibiting enhanced electrocatalytic properties for ORR. Furthermore, a combination of X-ray photoelectron spectroscopy (XPS) and electrochemical measurements was used to investigate the roles of various nitrogen states in ORR, and the contribution of amino group has been demonstrated for the first time. Our experiments show that the graphitic- and amino-type of nitrogen components determine the onset potential and electron transfer number, while the total content of graphitic and pyridinic nitrogen atoms is the key factor to enhance the current density in the electrocatalytic activity for ORR. This work could lead to economical synthesis of AG as efficient ORR electrocatalyst in fuel cells, and help to understand the catalytic mechanism of various nitrogen states towards ORR.

Introduction

Fuel cell is being considered as a promising renewable energy using hydrogen as source in recent years. Before fuel cells can be widely used as new products in the market, however, some issues need to be addressed, including the optimal choice of fuel, the development of alternative materials in the fuel-cell stack, as well as the efficient and inexpensive electrocatalyst triggered for cathodic oxygen reduction reaction (ORR) [1,2]. So far, Platinum (Pt)-based nanomaterials have been widely studied as active ORR

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catalysts, but suffer from multiple issues, e.g., poor durability, crossover, and poisoning effects, as well as the limited resource of Pt, which are hampering the wide commercialization of Pt-based catalysts for fuel cells [3,4]. Recently, intensive studies on metal-free catalysts have been aimed at reducing the cost and improving the performance towards ORR. However, there are still two tremendous challenges, including the inferior onset potential compared to Pt/C catalyst and unclear functions of various nitrogen states towards ORR [5-9].

Graphene, a single layer of sp^2-bonded carbon in a hexagonal lattice, has attracted more and more attention due to its fascinating properties and great promise in the fields of electronics, mechanics, and nanocatalysts [10-15]. One possible route to achieve more applications of graphene is to modulate its properties by chemical doping and modification [16]. For example, nitrogen-doped graphene (NG) was found to have enhanced electronic and catalytic properties than the intrinsic graphene, which can be used for nanodevices and fuel cells [17-19]. However, most of the N-doping approaches were complex and performed under harsh conditions, such as high temperature in gas phase, plasma state, arc discharge, and microwave treatment [20-22]. Recently, several solution-phase processes have been designed to scale up the production of NG [23-25]. In our previous work, we employed supercritical liquid-phase exfoliation to produce NG to modulate the electric properties of graphene [26]. The reduction of graphite oxide (GO) by hydrazine was also developed and widely used [27-29]. However, as a highly toxic and potentially explosive chemical, the use of hydrazine should be avoided in large-scale implementation [30]. Very recently, a wet chemical method was proposed to synthesize NG using dicyandiamide as nitrogen source, but more than 20% of oxygen content may significantly hinder its electrochemical performance [31]. A general and safe solution-phase synthesis of NG with high efficiency in ORR is still highly desirable. Moreover, amino-functionalized carbon materials are reported to have good catalytic activities very recently [32]. It is therefore interesting to combine the amino-modification and N-doping on the graphene structure, and the designed amino-functionalized NG (AG) may hopefully be a good metal-free catalyst for ORR in fuel cells.

Herein, we report three different kinds of graphene samples (AG, deaminated NG, and annealed NG) as metal-free catalysts for ORR. The successful introduction of amino species on graphene structure leads to the best performance in ORR, which indicates that amino N plays an important role in ORR. The effects of pyridinic, pyrrolic, and graphitic nitrogen functionalities have also been investigated systematically. We expect that our work would be useful to see the electrocatalytic process of nitrogen-containing carbon catalysts towards ORR.

Experimental

Materials preparation

All reagents are of analytical grade and used without further purification. GO was prepared from graphite powder by a modified Hummers method [33]. 1 g of graphite, 0.5 g of $NaNO_3$, and 23 mL of concentrated sulfuric acid were stirred together in an ice bath for 24 h. Under vigorous agitation, 3 g of $KMnO_4$ was slowly added. Subsequently, the solution was transferred to a 35-40 °C water bath and kept there for 30 min. Next, 46 mL of water was gradually added, and the solution was stirred for 15 min while the temperature was raised to 90±5 °C. Finally, the solution was diluted with 140 mL of water and treated with 5 mL of H_2O_2 (30%), turning the color from dark brown to yellow. The warm solution was filtered and washed with 5% HCl solution and then washed with water. The resultant solid was dried in a vacuum oven at 70 °C overnight.

Synthesis of AG: AG was synthesized through a one-pot solvothermal process. In a typical procedure, 80 mg of GO was added to 10 mL of water and sonicated for 0.5 h. Next, 70 mL of ammonia solution (25 wt% in water) was added, and the mixture was transferred into a 100 mL Teflon-lined autoclave and maintained at 200 °C for 12 h. The black solid was washed with 0.1 M HCl solution to remove the remaining ammonia solution and then washed repeatedly with water and ethanol. The final product was collected by centrifugation and dried at 60 °C overnight under vacuum to remove the physisorbed NH_3, and kept for further characterization.

Synthesis of chemically converted graphene (*CCG*): CCG was prepared by a common reduction approach with hydrazine as follows [34]. 160 mL of GO dispersion (1 mg mL^{-1}) was mixed with 0.8 mL of hydrazine (98% in water), and 80 mg of NaOH was added to adjust the pH value of the solution to 10. The mixture was stirred in an oil bath at 80 °C under a water-cooled condenser for 24 h. After reduction, the product was filtered and washed with 0.1 M HCl solution, water and ethanol, and finally dried in a vacuum oven at 60 °C overnight.

Synthesis of deaminated NG: Deaminated NG was prepared via a common chemical deamination process containing two steps: diazotization and hydrolysis. In a typical procedure, 20 mg of as-made AG was added to 10 mL of sulfuric acid (0.272 mmol) and sonicated for 30 min, yielding a black dispersion. Next, 5 mL of sodium nitrite solution (0.545 mmol) was gradually added, and the mixture was stirred in an ice bath for 15 min under vigorous agitation. 5 mL of urea solution (0.272 mmol) was then poured to remove the residual sodium nitrite, and the diazotized NG was transferred to sulfuric acid (3 M) for hydrolysis. For comparison, a part of pristine AG was treated with sulfuric acid (3 M), but without any other reagents. Finally, the products were washed repeatedly with water to remove the acid, and dried in a vacuum oven at 60 °C for 6 h.

Synthesis of annealed NG: Annealed NG samples were prepared by a simple annealing method under different temperatures (400, 600, 800, and 1000 °C). The resultant materials are referred as NG-400, NG-600, NG-800, and NG-1000, respectively. The detailed procedure is as follows: AG was put in a quartz boat in the center of a tube furnace. After flowing argon for 15 min, the furnace was heated to the designed temperature (e.g., 400 °C) at a constant heating rate of 10 °C min^{-1} and then maintained for 1 h under argon. The products were collected when the furnace temperature was below 50 °C.

Sample characterizations

X-ray diffraction (XRD) patterns were performed on a Philips X'Pert Pro diffractometer with Cu Kα (λ=1.5405 Å) radiation. Scanning electron microscopy (SEM) images were recorded on a Hitachi S-4800 SEM. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED)