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Full Length Article

Facile enhancement of the active catalytic sites of N-doped graphene as a high performance metal-free electrocatalyst for oxygen reduction reaction

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ABSTRACT

A simple and facile N-doping process has been developed to prepare graphene nanosheets with a high loading of active catalytic sites through the combination of hydrothermal and microwave processes. High resolution transmission electron microscopy, X-ray photoelectron spectroscopy and Raman analysis have been used to characterize the morphology and composition of the prepared materials. Also, linear sweep voltammetry (LSV) was conducted to investigate the electrocatalytic performance of the N-doped specimens toward oxygen reduction reaction (ORR). It was revealed that post-treatment of hydrothermally-treated N-doped graphenes under microwave irradiation in the presence of nitrogen precursor can result in the formation of a large content of quaternary nitrogen functionalities. Also, the LSV analysis revealed that fabrication of the graphene nanosheets under the proposed N-doping strategy resulted in potent electrocatalytic activity of graphene nanosheets toward ORR through a four electron pathway.

1. Introduction

Increasing of the ecological awareness and also depletion of petroleum resources over the past several years have guided the attentions toward development of more efficient and less polluting alternative power sources such as fuel cells [1,2]. However, the absence of efficient and cost-effective electrocatalyst materials for oxygen reduction reaction (ORR) is still a major challenge for practical commercialization of low temperature fuel cells and also metal-air batteries. Currently, Pt and Pt-based alloys are the most effective cathode materials for ORR [3]. However, these catalyst materials suffer from several drawbacks including high cost and limited supply of Pt resources which prevent the practical commercialization of the Pt-based cathode materials for ORR [1,4,5]. As a result, extensive researches have been conducted to explore alternative catalyst materials to replace or reduce the expensive Pt-based materials [4,6,7].

Graphene as a two-dimensional allotrope of carbon has attracted substantial interest due to its unique properties such as good chemical stability, high electrical conductivity, large specific surface area and also high mechanical strength [8–11]. Several studies have demonstrated that graphene possesses promising electrocatalytic activity toward ORR [12–14]. In addition, it has been found that doping of heteroatoms such as N, S, F and B into graphene matrix is a powerful technique to tailor the electrocatalytic performance of graphene derivatives [8,13,15–20]. In this regard, N-doping has been proposed as an effective strategy for enhancement of graphene catalytic activity [21]. Also, it has been demonstrated that the type of nitrogen functionality and its concentration plays a significant role in the electrocatalytic activity of the N-doped graphene materials [21,22]. However, there have been contradictory reports about the impact of various nitrogen functionalities. In this regard, while most studies have demonstrated that quaternary N is an effective promoter for catalytic activity of graphene toward ORR [23–26], there have been several reports which claimed that pyridinic nitrogen is the desirable nitrogen functionality for ORR [27–30]. As a result, the use of N-doped graphene nanosheets for ORR is still a new topic and need further investigation.

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In order to improve the performance of graphene for ORR, it is necessary to increase the content of desired nitrogen functionalities. Currently, various techniques have been developed to prepare graphene nanosheets with various nitrogen functionalities including pyridinic, pyrrolic and quaternary nitrogen species. Development of synthesis procedures which provide a proper control over type and concentration of N species is very useful and imperatively demanded. Hydrothermal process has been widely used to prepare N-doped graphene. This process provides a relatively low temperature range for nitrogen doping and often results in the formation of a large content of pyridinic and pyrrolic nitrogen functionalities which are more stable at lower temperatures [31]. On the other hand, quaternary nitrogen is formed via substitution of carbon with nitrogen atoms at the basal plane of graphene network and often occurs at elevated temperatures [32]. Microwave irradiation has been widely used as a simple, facile and efficient heating process to develop microwave-assisted synthesis techniques [3,33,34]. It can provide several advantages including fast, volumetric and uniform heat transfer to the reactants and thereby causes a homogeneous synthesis condition at elevated temperatures. Several studies have reported the use of microwave heating for N-doping reaction [23,35].

In this study we aim to develop a simple strategy to enhance the formation of quaternary N dopant in graphene network through the combination of hydrothermal and microwave-assisted synthesis procedures. Accordingly, the mixture of graphene and N precursor is initially subjected to hydrothermal treatment to prepare N-doped graphene. In the next step, the hydrothermal-treated graphene sample would be further mixed with nitrogen precursor and subjected to microwave annealing to enhance the formation of quaternary N and simultaneously results in transformation of the pyrrolic N to quaternary N [31]. Since solid state microwave irradiation provides elevated temperatures, it is anticipated that post-treatment of a mixture of hydrothermal-treated N-doped graphene and nitrogen precursors under microwave irradiation would result in the formation of a high content of quaternary N species. Also, N-doped graphene samples that prepared separately by simple hydrothermal treatment and by simple microwave irradiation were compared with those obtained by the combination of both methods for ORR.

2. Materials and methods

2.1. Synthesis of nitrogen-doped graphene samples

In order to investigate the effect of doping procedure on the electrocatalytic performance of graphene samples, N-doped graphenes were prepared under various N-doping conditions. In this regard three different doping processes including solid state microwave method, hydrothermal method and combination of hydrothermal and microwave methods (two-step process) were employed to prepared N-doped graphene samples. Urea (Merck) was used as nitrogen precursor. Also, commercially available few-layered graphene particles were obtained from Angstron Materials (N002-PDR).

The microwave doping of graphene samples was conducted by microwave irradiation of a mixture of graphene and urea. In this regard, a solid mixture of graphene and urea with the weight ratio of 1:25 was prepared and thoroughly mixed in an agate mortar to give a uniform blend. The mixture was then subjected to microwave irradiation in a household microwave oven (LG, 900 W, 2450 MHz) for 5 min. The product was then thoroughly washed with distilled water to remove the remaining impurities and dried by using a freeze dryer. Finally, the resulting solid was collected and ground down to give a powder product.

For hydrothermal N-doping process, an aqueous suspension of graphene and urea precursors was prepared and heated under hydrothermal condition. In a typical experiment, a mixture of graphene and urea with the weight ratio of 1:25 was uniformly blended to prepare a uniform admixture. Then 1 g of the prepared blend was added to 25 mL of distilled deionized water and sonicated for 3 h to give a uniform suspension. In the following, the prepared slurry was transferred to a Teflon lined hydrothermal synthesis autoclave reactor and subjected to the hydrothermal treatment at 180 °C for 12 h. The product was then thoroughly washed with distilled water to remove the remaining unreacted chemicals and dried by using a freeze dryer.

The two-step N-doping procedure consists of two steps. In the first step, the graphene and nitrogen precursor blend was prepared and treated as described for the simple hydrothermal process. In the next step, the resulting product of the hydrothermal process was used as starting precursor for microwave doping and heated under microwave irradiation with the same parameters as mentioned in the microwave method.

2.2. Characterization of N-doped graphene powders

The surface composition and valence states of graphene and N-doped graphene samples were analyzed by X-ray photoelectron spectroscopy. The XPS analysis was conducted by using an UHV multipurpose surface analysis system (ESCALAB 250Xi, Thermo, UK) operating at base pressures of $<10^{-10}$ mbar. The photoelectron spectra were obtained with an Al Kα (1486.6 eV) anode operating at a constant power of 300 W (15 kV and 20 mA). During the spectra acquisition, the constant analyzer energy (CAE) mode was employed at pass energy of 20 eV and a step of 0.1 eV. Deconvolution and curve-fitting of the XPS spectra were carried out using the Avantage software.

Also, morphology of the graphene and N-doped graphene materials were measured with both high resolution transmission electron microscopy (HR-TEM) and field emission scanning electron microscopy (FE-SEM). Transmission electron microscopy investigations were carried out by using a HF-3300 HR-TEM microscope (Hitachi, Japan) operating at 300 kV and also field emission scanning electron microscopy was conducted by using an S-4800 FE-SEM microscope (Hitachi, Japan).

Raman studies were recorded by using a monocromator (NICOLET ALMECA XR, Thermo, USA). Excitation was carried out with a 532 nm line from an argon ion laser. Each spectrum consisted of 16 accumulations averaged together and their resolution was 0.5 cm^{-1}.

2.3. Electrocatalytic performance of N-doped graphenes

The linear sweep voltammetry (LSV) measurements were conducted to characterize the electrocatalytic performance of the N-doped specimens toward ORR in an oxygen saturated 0.1 M KOH solution. The electrochemical measurements were conducted with a three electrode cell system by using an Autolab potentiostat/galvanostat (Model Type 3). An Ag/AgCl (3 M KCl) electrode and a platinum rod were used as reference and counter electrodes, respectively. Also, working electrode was a thin layer of Nafion-bonded catalyst ink which was drop casted on the surface of a glassy carbon electrode (5 mm in diameter). In order to prepare the working electrode, 2 mg of the catalyst powder was uniformly dispersed in a mixture of ethanol with 10 percent of Nafion solution (5 wt.%) to prepare a homogeneous catalyst suspension containing 10 mg ml^{-1} of catalyst powder. Then, the required amount of catalyst ink was transferred to the surface of a well cleaned and polished glassy carbon electrode. The loading of