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Chemoselective solution synthesis of pyrazolic-structure-rich nitrogen-doped graphene for supercapacitors and electrocatalysis

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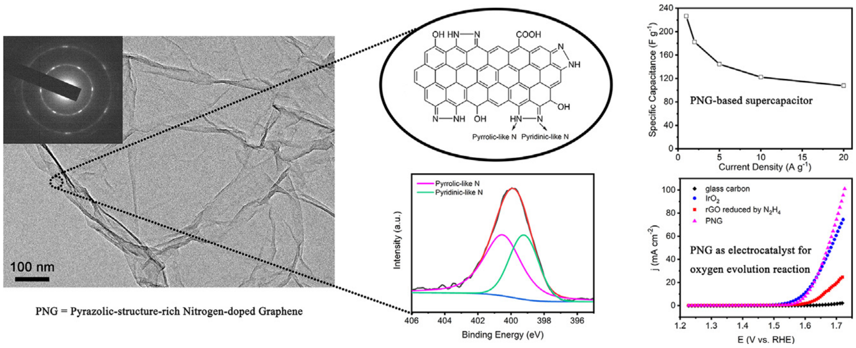
HIGHLIGHTS

- Low-T solution synthesis of Pyrazolic-structure-rich Nitrogen-doped Graphenes (PNG).
- PNG shows ultrathin few-layer graphene structure with hydrophilic groups at edges.
- PNG supercapacitor exhibits outstanding capacitance, energy density and durability.
- As an electrocatalyst for OER, PNG shows higher activity and stability than IrO_2.

GRAPHICAL ABSTRACT



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ABSTRACT

Nitrogen doping is an effective way to tailor the properties of graphene-based materials. Current synthetic methods for nitrogen-doped graphene (NG) are limited by poor selectivity on nitrogen bonding configurations in the NG materials. Herein, we report the chemoselective synthesis of Pyrazolic-structure-rich Nitrogen-doped Graphene (PNG) in water solutions. PNG exhibits outstanding capacitive and electrocatalytic activities. The PNG supercapacitor with acidic hydrogel electrolytes provides a specific capacitance of 226 F g^{-1}, an energy density of 30.3 Wh kg^{-1} and great durability, outperforming most of previous carbon materials-based supercapacitors. With neutral hydrogel electrolytes, the PNG supercapacitor can be operated at higher voltages up to 1.4 V, providing an enhanced energy density of 35.8 Wh kg^{-1}. As an electrocatalyst for oxygen evolution reaction (OER) in alkaline solutions, PNG needs a low overpotential of 394 mV to drive 20 mA cm^{-2} current density and retains its activity for 16 h without any decay. The activity and durability of PNG are superior to that of noble-metal-based OER catalyst IrO_2. Our results demonstrate a facile and scalable chemoselective synthesis of high-performance bifunctional NG for supercapacitors and electrocatalysis.

1. Introduction

Carbon-based materials have attracted great interests for applications in energy conversion and storage, such as the 2D and 3D porous carbon materials [1–5], CNTs [6] and graphene. In general, graphene has been regarded as one of the most promising electrode material, due to its excellent properties such as high electrical conductivity, large specific surface area and excellent chemical stability [7–9]. Many

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efforts have been made to change graphene's chemical and physical properties by modifying its structure and morphology [10]. Nitrogen doping is an effective way to tailor the properties of graphene [11,12]. In nitrogen-doped graphene (NG), the charge distribution of carbon atoms is tuned by the neighbor nitrogen atoms [13], which induces "active region" that can participate in catalytic reactions, such as the oxygen reduction reaction (ORR) [14,15] and oxygen evolution reaction (OER) [16,17]. In addition, NG can also be used as active electrode materials for supercapacitors [18–22] and batteries [23–26] with enhanced performance.

Three bonding configurations of nitrogen are commonly observed in NG: pyridinic-N, pyrrolic-N and graphitic-N [27]. Recent studies suggest that the type and content of nitrogen bonding configurations in NG play crucial roles in determining the performance of NG for electrocatalysis [28] and supercapacitors [29]. For electrocatalysis, the electron-donating graphitic-N sites can function as active sites for ORR, whereas the electron-withdrawing pyridinic-N sites are suggested as active sites for OER [28]. For supercapacitors, it is suggested that both pyridinic-N and pyrrolic-N have contribution to the pseudo-capacitance of NG [30]. Therefore, chemoselective synthesis of NG with desired type and content of nitrogen bonding configurations could help to enhance the performance of NG and explore the structure-property relationship of NG [10].

Currently, NG can be prepared by direct synthesis or nitrogen doping of graphene oxide (GO). Direct synthesis methods include chemical vapor deposition (CVD), segregation growth, solvothermal reaction and arc-discharge approach, which are typically limited by small production scale and high cost [31]. The methods of doping nitrogen into GO, including thermal treatment [32], plasma treatment [33], hydrothermal reduction [34] and N_2H_4/NH_3 reduction of GO [35], can provide a larger scale production of NG than direct synthesis methods. However, current methods for NG synthesis can hardly control the type and content of nitrogen bonding configurations in NG. Most of these methods also need sophisticated equipment and/or harsh reaction conditions such as high temperature, high pressure, vacuum or plasma, which hinder the massive production and applications of NG at low cost.

Herein, we sought to develop a chemoselective synthesis method to introduce nitrogen into GO through defined organic reactions. Recent studies indicate there is a considerable content of α,β-unsaturated ketone structure in GO [36,37]. Inspired by the convenient ring formation reaction between aminoguanidine and α,β-unsaturated ketone to form pyrazole [38], we propose to use aminoguanidine to introduce pyrazolic structure into GO at a mild condition (Scheme 1). After the ring closure, the guanidine groups could be easily hydrolyzed in alkaline solution [39]. At the meantime, aminoguanidine could reduce the epoxide groups in GO to restore the π-conjugated structure of graphene, while some hydroxyl and carboxylic groups in GO are reserved to retain a certain degree of hydrophilicity. The formed pyrazolic structure in the obtained Pyrazolic-structure-rich Nitrogen-doped Graphene (PNG) consists of two different types of N atoms: one type is pyridinic-like and the other is pyrrolic-like (Scheme 1). Therefore, we expect PNG could behave as bifunctional active materials for both supercapacitors and electrocatalysis.

Indeed, PNG exhibits outstanding capacitive and electrocatalytic activities, due to its high content of nitrogen doping (9.6 wt%), ultrathin graphene sheet structure, high specific surface area and stable distribution in aqueous solution. The PNG-based supercapacitor with acidic hydrogel electrolyte provides a high specific capacitance of $226\,F\,g^{-1}$ and a high energy density of $30.3\,Wh\,kg^{-1}$, which can be further enhanced to $295\,F\,g^{-1}$ and $39.7\,Wh\,kg^{-1}$, respectively, after an activation process by long-term charge-discharge cycling. With neutral hydrogel electrolytes, the PNG-based supercapacitor can be operated at higher voltages up to 1.4 V, with a specific capacitance of $135\,F\,g^{-1}$ and energy density of $35.8\,Wh\,kg^{-1}$. PNG-based supercapacitors exhibit superior capacitive performance than previously reported graphene-based and NG-based supercapacitors. As an active electrocatalyst for OER in alkaline solution, PNG needs a low overpotential of 394 mV to drive $20\,mA\,cm^{-2}$ current density and retains its activity for at least 16 h without any decay. The activity and durability of PNG as OER electrocatalyst are superior to that of noble-metal-based catalyst IrO_2. The outstanding performance enables PNG as a bifunctional active material for supercapacitors and electrocatalysis.

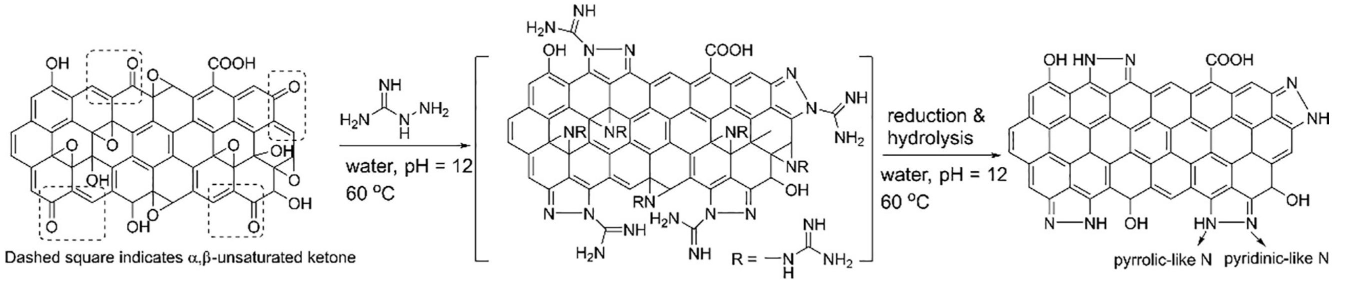
2. Materials and methods

2.1. Reagents and materials

Natural graphite was purchased from Qingdao Graphite Company. Polyvinyl alcohol (PVA, 99% hydrolyzed, degree of polymerization 1750), aminoguanidine hydrochloride, hydroxylamine hydrochloride, sodium sulfate and potassium permanganate were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. Carbon cloth (thickness: 0.36 mm) was purchased from Shanghai HESEN Electric Co., Ltd.

2.2. Synthesis of graphene oxide (GO)

Graphene oxide was synthesized by using a modified Hummer's method [40]. Briefly, flaky natural graphite (2.0 g) was added to a 250 mL flask containing the mixture of 135 mL concentrated sulfuric acid (98%) and 15 mL phosphoric acid (70%). The mixture was cooled in an ice-water bath. Potassium permanganate powder (12.0 g) was slowly added to the mixture using stirring. Then the mixture was transferred to a 50 °C water bath and stirred for 24 h. The muddy product was carefully transferred to centrifuge tubes and centrifuged at 5000 rpm for 30 min. The top layer liquid was carefully decanted as waste acid. The red muddy solid on the bottom was transferred into a 250 mL flask in an ice-water bath. 100 mL ice water was added to the flask, followed by the addition of hydroxylamine hydrochloride



Scheme 1. A schematic illustration of pyrazole formation at the edge of GO platelets in the reaction between aminoguanidine and GO. The epoxide groups in GO are reduced by aminoguanidine to restore the π-conjugated structure of graphene. The α,β-unsaturated ketone indicated by dashed squares can react with aminoguanidine to form pyrazolic structure. After forming the pyrazole ring, the guanidine group can be easily hydrolyzed in alkaline solution. Some hydroxyl and carboxylic groups are reserved to maintain the hydrophilic property of PNG.