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Facile chemical synthesis of nitrogen-doped graphene sheets and their electrochemical capacitance

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HIGHLIGHTS

- N-doped graphene (NGS) is simultaneously reduced from GO and functionalised at 80 °C.
- The reduction and N-doping of GO occur in 1 wt.% ammonia water at atmosphere pressure (101,325 Pa).
- NGS has a N composition of 4.4 at.% and exhibits higher thermal stability than GO.
- Specific capacitance of NGS is nearly twice that of RGO without N-doping.
- NGS exhibits a maximum specific capacitance of 233.3 F g^{-1} and superior cycling stability.

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ABSTRACT

To improve the electrochemical performance of graphene materials, nitrogen-doped graphene sheets (NGS) were simultaneously reduced and functionalized with nitrogen (N) doping from graphene oxide (GO) by a simple process using 1 wt.% ammonia water solution as the reducing agent, nitrogen precursor and solvent. The NGS were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy–energy dispersive spectroscopy microanalysis, and differential scanning calorimetry. The thermal stability of NGS was much higher than that of GO. The N content in NGS was 4.4 at.% and a maximum specific capacitance up to 233.3 F g^{-1} was obtained at 0.5 A g^{-1}. At 0.02 V s^{-1}, the NGS exhibited a specific capacitance of 140.3 F g^{-1}, which was over 8 times that of GO and nearly 2 times that of graphene without N-doping. These results revealed that N-doping of functional graphene provide remarkable improvements on the electrochemical capacitive performance of graphene materials. The NGS also showed high cycle stability of capacitive performance.

1. Introduction

Recently, the development of capacitors with high energy and power densities, and lower fabrication costs have attracted much interest due to the growing demand for portable electric systems and hybrid electric vehicles. Carbon materials are common electrode materials for electrochemical capacitors [1–3]. To improve their electrochemical performance, the introduction of a heteroatom, such as nitrogen (N), has been verified as a promising approach. Two conventional methods have been usually used to synthesize N-doped carbon materials. One is by direct N-doping during the growth of the carbon materials [4–7], and another is by thermal treatment of the N-containing polymers [8–11]. A high temperature environment is often required for both methods, and thermally stable products with poor wettability and low chemical activity are always obtained. Besides these two methods, the introduction of nitrogen into carbon materials can also be achieved by modifying the N-containing organic groups through a wet chemical method, which usually comprises two steps: (a) creation of carboxylic acid groups on the surface of carbon materials; and (b) amidation [12–14]. Compared to pristine carbon materials, nitrogen-modified carbon products obtained by this method have higher chemical activity and affinity to other molecules and polymer systems.

As a recently developed carbon material, graphenes have attracted increasing attention owing to their two-dimensional nanostructure, extraordinary electrical and thermal characteristics, superior

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mechanical properties, and potential low production cost. These functional properties render them suitable materials for many advanced engineering applications [15–19], such as electrode materials for high performance electrochemical capacitors. Graphenes can be prepared by the chemical reduction of graphene oxide (GO) with many reducing agents, e.g., hydrazine [19–21], sodium borohydride [22,23] and ethylene glycol (EG) [17,18]. It is well known that these chemicals are hazardous to human health and the environment; for example, hydrazine, hydrazine hydrate and sodium borohydride are highly poisonous and explosive materials [24]. Hence, it is desirable to achieve GO reduction by more environment-friendly agents, and to prepare functional graphenes with high electrochemical performance by N-doping. Two main methods have been developed to achieve this goal. One is by thermal treatment of GO with urea at high temperature, normally above 600 °C [25,26]. Another is by hydro- or solvo-thermal treatment of GO in the presence of concentrated ammonia water [27] or organoamine [28]. Although hydro- or solvo-thermal reaction can occur at lower temperature (normally over 100 °C), the pressure of the reaction system inside of the autoclave is inevitably much higher than that of the outside and is sometimes difficult to control. Herein, a simple and mild method to fabricate N-doping of graphenes directly from GO in a very dilute ammonia water (~ 1 wt.%) is presented. With this method, the reduction of GO with ammonia water and the N-doping of graphene are expected to be achieved simultaneously under mild experimental conditions. The method is distinctly different to previous reported solvo-thermal treatment of GO with EG and ammonia water [17], where EG is used as reducing agent and solvent, and ammonia water serves merely as nitrogen precursor. More importantly, the preparation reaction can be conducted only at 80 °C at atmosphere pressure (that is, 101,325.00 Pa), a much milder experimental condition compared to the high temperature at 180 °C in an autoclave with unknown pressure [17,27,28]. Also, a very high concentration of ammonia water (28 wt.%) is used in the hydrothermal method [27]. Since all these previous methods to N doped graphene sheets (NGS) require energy-intensive batch process and special equipment or expensive reagents, the present method is, by contrast, energy-efficient, economical and capable of industrial scale-up. The capacitance performance of NGS has been studied mainly in alkaline solutions [26–28]. In this work, the electrochemical capacitive behaviour of NGS in acid electrolyte will be investigated. To study the effect of the chemical reduction and N-doping on the electrochemical performance of graphene materials, GO and reduced GO using sodium borohydride will also be prepared and their electrochemical properties compared with those of NGS.

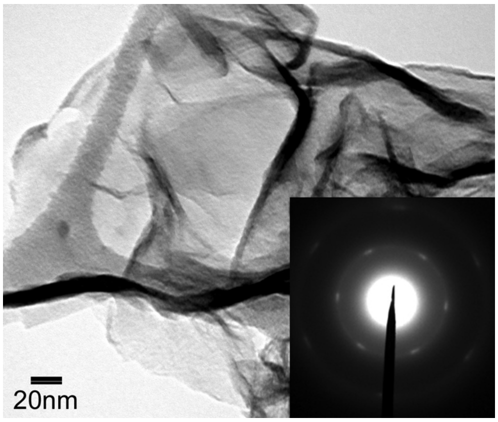

Fig. 1. Transmission electron microscopy image of NGS. Inset is its selected area electron diffraction pattern.

2. Experimental

2.1. Materials

Graphene oxide was prepared from natural graphite powder using a modified Hummers [29] method. 10 g of graphite powder was mixed with 230 mL cold (at 0 °C) concentrated H_2SO_4 (98 wt.%). Then, 30 g $KMnO_4$ was added gradually into the mixture with stirring and cooling to keep below 20 °C. Subsequently, the final mixture was stirred around 35 °C for 0.5 h. 460 mL distilled water was then added slowly and the mixture was held at ~98 °C for 0.25 h. The reaction was terminated by adding 1400 mL distilled water and 100 mL 30 wt.% H_2O_2 solution. The mixture was filtered and successively washed with 5 wt.% HCl aqueous solution until no sulphate could be detected with $BaCl_2$ and then dried at 60 °C in a vacuum oven.

To prepare N-doped graphene, 0.25 g GO was added to 260 mL of ~1 wt.% ammonia water (diluted from 28 wt.% ammonia water with distilled water) via ultra-sonication. This solution was stirred at 80 °C for 6 h. After the reaction, the solution was filtered and the

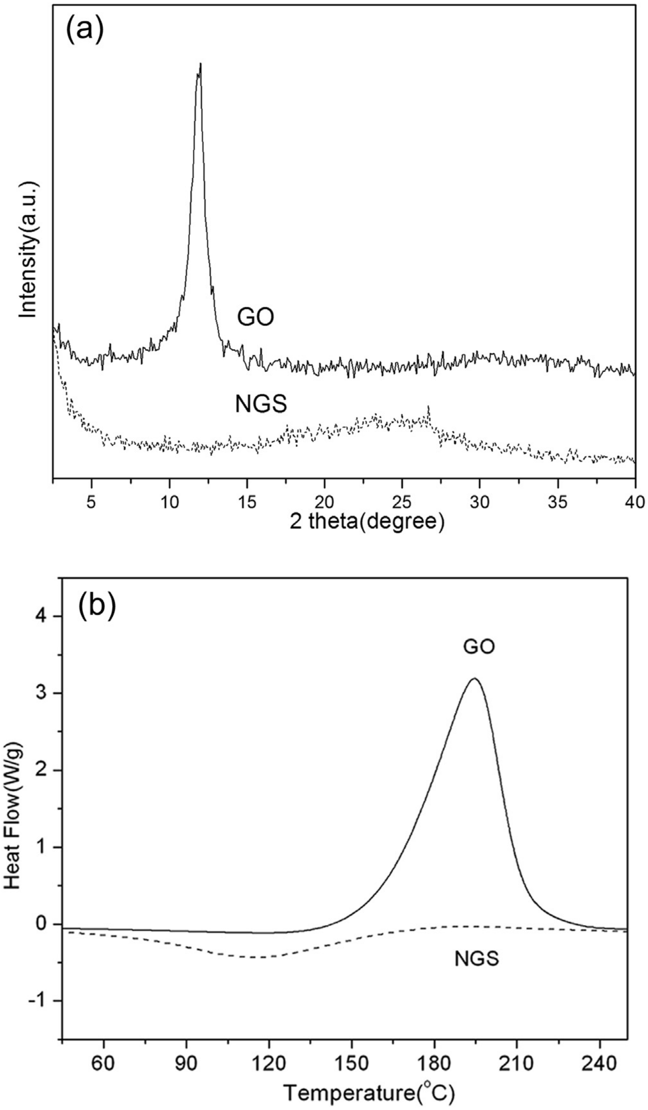

Fig. 2. (a) X-ray diffraction patterns; and (b) differential scanning calorimetry curves of GO and NGS.