High-performance supercapacitor of macroscopic graphene hydrogels by partial reduction and nitrogen doping of graphene oxide

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ABSTRACT

In this work, the 3D macroscopic graphene hydrogels (MGHs) with a high capacitor performance were easily prepared by a one-step hydrothermal method from graphene oxide (GO) dispersions. A very small amount of 1,4-butanediamine was employed to realize the partial reduction of GO, modification of the 3D structure of MGHs, and nitrogen doping of graphene, at the same time. The synthesized MGH-6 sample in the wet state exhibit a high specific capacitance of 268.8 Fg^{-1} at 0.3 A g^{-1} in 6 M KOH electrolyte, and this capacitance can be maintained for 84.9% even as the discharging current density was increased up to 10 A g^{-1}. The MGH-6 sample also shows good cycle stability along with a 1.03% increase of its initial specific capacitance after 10000 cycles at current density of 10 Ag^{-1}. These remarkable properties are ascribed to the both nitrogen- and oxygen-containing functional groups, modified macroporous 3D framework, and the high specific surface area of the graphene. Combining with the economical and easy path toward mass production, the present MGH-6 can be expected as a promising candidate for high-performance supercapacitors.

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1. Introduction

Graphene is composed of 2D single layer carbon atoms arranged in a hexagonal structure. As a novel carbon materials, graphene has superior electrical conductivity, large specific surface area, excellent thermal conductivity, and other excellent chemical and physical properties [1–4]. All these advantages make graphene meet the requirements of various applications, such as sensors, batteries, electrocatalysis and supercapacitors [5]. The single-layer graphene with a specific area of ∼2600 m^{2}g^{-1} and its theoretical capacitance is 550 Fg^{-1}, so it has replaced other carbon materials as the main research hotspot in the field of supercapacitors [6]. Graphene can be produced by several methods, such as mechanical exfoliation, liquid phase exfoliation, chemical vapor deposition (CVD), chemical reduction, and so on [7–10]. Nevertheless, some problems still restraining its practical application in supercapacitors, like mass production and serious aggregation and restack of graphene [11]. These obstacles lead to graphene materials display much lower capacitance than their theoretical value. For the purpose of preventing the restack of graphene sheets and improving the performance of graphene-based device, many methods have been proposed, including refinement of porosity in graphene, development of graphene-based composites, and doping graphene with heteroatom [12–14].

Self-assembly of 2D flexible graphene sheets is a good method to fabricate 3D macroscopic graphene frameworks [15]. Owing to the pore sizes of such architectures are in the range from sub-micrometer to several micrometers, 3D macroscopic graphene architectures present special properties, like exceptional mechanical property, excellent electrical property, ultralight, high specific surface area and abundant pore channels. The 3D macroscopic architecture could prevent graphene sheets from aggregating and restacking in the course of assembling as well as provide sufficient contact area between the electrolyte and electrode [11]. Furthermore, 3D porous framework endows high-rate ions diffusion and provides multidimensional electrons transport pathways, which will lead to outstanding electrochemical performance [16].

Doping graphene with foreign atoms can tailor its electronic properties, modulate surface chemistry and adjust the chemical composition of graphene [17]. Among various chemical elements for doping, nitrogen is regarded as one of the most promising dopant since it has similar electron numbers and comparable

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atomic radius with carbon [18]. N-doped graphene (NG) generally has three kinds of nitrogen species, including pyridinic N, pyrrolic N and graphitic N. Pyridinic N and pyrrolic N in NG can improve pseudocapacitance of doped graphene because of pseudo-faradaic reactions, whereas graphitic N can improve the electrical conductivity of doped graphene, which will facilitates the electron transfer [19]. Therefore, NG can not only improve the pseudocapacitance but also enhance the cycle life of supercapacitors. NG can be synthesized by different methods, such as CVD, thermal annealing, plasma, arc-discharge and so on [20]. However, these methods suffer from rigorous reaction conditions and special apparatus, resulting in low products yields and high energy consumption [21]. In contrast to these processes, the hydrothermal approach has advantage of mild conditions and large-scale production. In previous reports, high level N-doped graphene is desirable for all kinds of electrical devices [22]. However, large amounts of dopants were needed when synthesis of NG, leading to such problems as low efficiency, high cost and environmental pollution.

It is well known that, there are a lot of oxygen functional groups in GO, such as epoxy, hydroxyl, quinone, carboxyl and carbonyl groups. These oxygen functional groups are beneficial, as they can enhance the capacitance by pseudocapacitive effects and improved the wettability of GO [23]. However, the use of GO as supercapacitor electrode materials was limited by its low conductivity. We would expect that partially reduced GO with small amount of organic amine could retain some sorts of oxygen functional groups

and introduce N atoms into the graphene lattices, which would improve the conductivity and give the reduced graphene oxide a combined effect of nitrogen- and oxygen-containing functional groups on its electrochemical performance in supercapacitors.

1,4-Butanediamine has relatively long molecular chain and two amino-groups, so we expect that the molecular chain can attach onto the plane of graphene by amine reactions with oxygen-containing groups at the surface of the GO and then inhibit the π-π stacking in the single graphene sheet. Furthermore, the other amino of the molecular chain can generate hydrogen bond with oxygen-containing groups, thereupon expand the space between the graphene sheets.

In this paper we present a facile one-step hydrothermal method for the preparation of high property 3D macroscopic graphene hydrogels (MGHs) as a supercapacitor electrode materials using GO and 1,4-butanediamine as precursors, which provides a promising option for low cost mass production. Scheme 1 shows the reaction mechanism sketch of MGHs. During the hydrothermal process, 1,4-butanediamine acts not only as a reduction agent to remove the oxygen functional groups of GO but also as a modification agent to adjust the inner structure of MGHs. Besides, 1,4-butanediamine can act as nitrogen source to realize the nitrogen doping. Therefore, the as-prepared MGHs samples are expected to have 3D framework, high specific surface and combined effect of nitrogen- and oxygen-containing functional groups, and as a result, the performance of the supercapacitors could be enhanced.
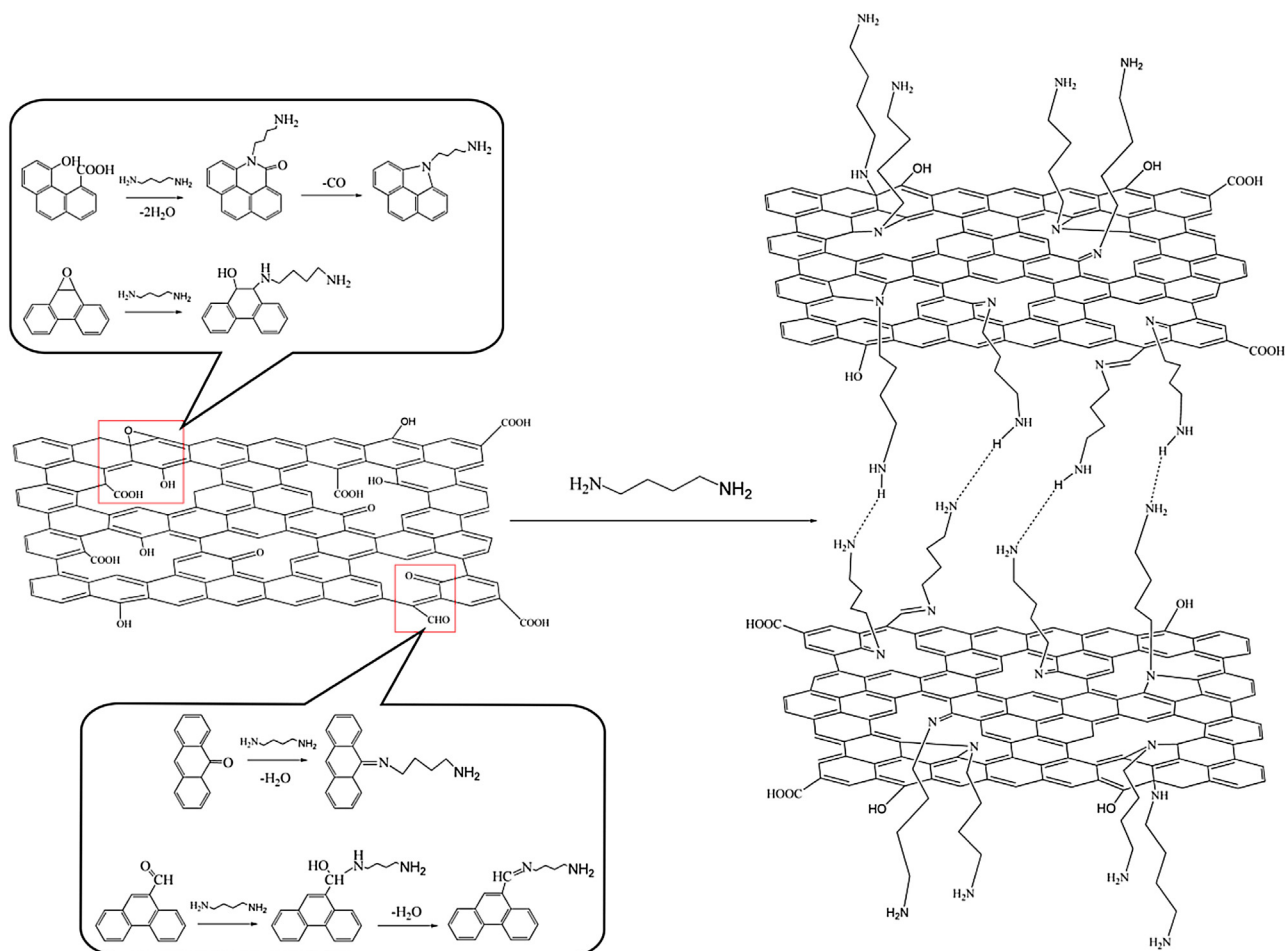
Scheme 1. Illustration of the possible reaction mechanism of the MGHs.