Sulfur/Nitrogen Dual-doped Porous Graphene Aerogels Enhancing Anode Performance of Lithium Ion Batteries

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ABSTRACT

Sulfur/nitrogen dual-doped graphene aerogels (SNGAs) with a unique porous network structure have been designed through a facile and versatile one-pot hydrothermal strategy. When employed as anode in LIBs, the SNGAs with nitrogen content of 1.50 wt.% and sulfur content of 15.11 wt.% exhibit superior cycle life and rate capability. For example, a high reversible capacity of 1109.8 mAh g^{-1} can be obtained after 400 cycles even at a high current density of 800 mA g^{-1}. It was discreetly demonstrated that the prominent improved performance of SNGAs can be mainly ascribed to the effect of dual-doping heteroatoms in cooperation with each other in to the graphene lattice as well as the porous nanostructure facilitating the mass transfer for both ions and electrons. Our conclusions illustrate that the strategy of dual-doped graphene aerogel may promote the potential application of graphene for high performance lithium ion batteries.

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1. Introduction

As one of the most effective energy storage devices, lithium ion batteries (LIBs) have been playing an exclusive role in portable electronic devices and energy device, due to their high energy density, long cycling life as well as sustainability, providing promise energy power instead of fossil fuels [1]. Currently, the application of LIBs widely extended form mobile phones to electric vehicles (EVs) exhibiting strengthening momentum in rechargeable battery markets [2,3]. However, the graphite as an anode material of commercial LIBs possesses a relatively low theoretical specific capacity (∼372 mAh g^{-1}). It is well known that increasing lithium storage capacity and enhancing rate capability are the two keys to optimize the properties of anode materials [4–6]. Graphene aerogels (GAs), a new class of ultralight and porous carbon materials, have been well-recognized by extensive investigation in the past few years. With its fascinating mechanical, thermal and electrochemical speciality, GAs have shown great potentials to optimize anode performance in LIBs [7–9]. Particularly, in view of the highly electrical conductivity with combination of 3D porous architectures, GAs can provide multidimensional electron transport pathways, increase the contact area of electrode/electrolyte, and reduce the transport distances for both ions and electrons, which can significantly improve the energy/power density of LIB system [10,11]. More importantly, heteroatom doping (such as S, N, B and P) has been demonstrated to be a pivotal strategy to optimize graphene performance due to the further enhanced electronic conductivity and Li$^+$ storage sites [12–15]. It has been reported accordingly that hole doping levels of single-layer graphene transistor can topped at to 5×10^{13} cm^{-2} [16]. Nitrogen (N) atomic has a similar size but discriminating electro negativity with carbon atomic (C: 2.55; N: 3.04). As a result, nitrogen-doped graphene (NG) has been wildly investigated and supposed to modify the graphene-based anode materials of LIBs [17,18]. As previously reported by our group, the nitrogen-doped graphene with 2.8 at.% nitrogen content as anode for LIBs displays superior electrochemical performance (684 mAh g^{-1} was retained at a current density of 100 mA g^{-1} after 500 cycles) over pristine graphene [19]. Note that the electrochemical performance of nitrogen-doped graphene

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materials can be further optimized by regulating the synthetic method and/or the doped content. For instance, Cai et al. stated that the higher content (about 7.04 at.%) of nitrogen embedded in graphene via thermal annealing results in better performance [20]. However, the graphene material with single element doping inevitably confront the performance bottlenecks as a result of the limited capability of graphene to accommodate single heterogeneous atom. Therefore, the strategy of dual-doped graphene has been well documented to be a more promising way to promote the electrochemical performance of graphene [21]. It is due that the opening band-gap and the defects caused by the introduction of nitrogen and sulfur atomics endow graphene with improved electrical conductivity and promoted electrochemical reaction active sites [22,23]. The increased lithium storage performance benefits from the matching electronic structure as well as the consequent structural defects of dual-doped behavior. For example, Zhuang et al. obtained co-doped carbon materials with the elemental content of 12.36 mas.% N and 2.40 mas.% S, when conducted at $100\,mA\,g^{-1}$ after 50 cycles, this materials can sustain a higher reversible capacity of $675.1\,mAh\,g^{-1}$ than undoped samples [24]. Unfortunately, a direct correspondence between Li^+ storage behavior and the remarkable contribution of dual-doping atoms has been rarely established. Therefore, there is still a great desire to develop an easy, effective, and extensible approach for refining the surface defects of graphene caused by N/S dual-doping, and illuminate the defects with relation to its electrochemical performance.

Herein, we designed three-dimensional (3D) S/N dual-doped monolithic graphene aerogels (SNGAs) via a simple and facile one-step hydrothermal method, which can precisely control the doping ratio and level of diverse heteroatoms. Additionally, compared with organic doping agent [4] and other dopants (such as, ammonium persulfate) [25,26], which may cause long-term adverse effects in the environment and high cost, thiourea as the single doping agent for sulfur/nitrogen source is little toxic to organisms. Moreover, some doping strategies inevitably consist of post-treatment at high temperature [4,25]. In this study, a simple and facile one-step hydrothermal approach was proposed to obtain S/N dual-doped porous graphene aerogels without post-treatment. The as-prepared SNGA samples possessing 3D interconnected frameworks with a porous architecture and crumpled surface are favorable for ion diffusion and electron transport. Additionally, the dual-doped of N and S atoms in graphene lattice exert characteristic synergistic effect, including more defects and advantageous electronic structure, which will promote the electrochemical performance of the graphene anode for LIBs. Our study successfully reveals the synergistic effect of dual-doping and will promote graphene materials for further applications in LIBs.

2. Experimental

2.1. Materials

Graphite powder (purity $\geq$ 99.95%), particle diameters of about 1.3 μm was produced from Aladdin (Shanghai, China). Other chemical reagents, such as $KMnO_4$ (99%), $NaNO_3$ (99%), concentrated sulfuric acid (95% ~ 98%), hydrochloric acid (36 ~ 38%), H_2O_2 (30%), and thiourea were supplied by Tianjin FengChuan Chemical Reagent Technology Ltd. (China). The chemicals were all analytical reagents.

2.2. Synthesis of graphene aerogel (GA) and S- and N-doped graphene aerogel (SNGA)

The synthesis of graphite oxide derived from natural graphite via a modified Hummers' method, as previously reported by our group [27]. In a typical experiment, graphene oxide (GO) aqueous suspension was obtained by ultrasonic of the resultant graphite oxide in deionized water for 30 min. Then the desirable brown dispersion was centrifuged for 30 min at 10000 rpm to remove impurities. Subsequently, different amounts of thiourea was added into the GO suspension under vigorous stirring for 30 min, the as-prepared suspension was transferred into a Teflon-lined autoclave with a 50 mL volume and maintained at 180 °C for 24 h. Then, the as-obtained product was filtered and washed by distilled water repeatedly. Finally, the products were freeze-dried to obtain SNGAs. The resultant materials synthesized by adding GO and thiourea with different ratio of 1:10, 1:20, 1:30 1:50 and 1:100 were labeled as SNGA-I, SNGA-SI, SNGA-II, SNGA-SII and SNGA-III, respectively. For comparison, the product without additive of thiourea was synthesized under the similar condition, which was labeled as GA-I.

2.3. Materials characterization

The powder XRD data was checked out by an X-ray diffractometer (D8 Advance of Bruker, Germany) with Cu/Kα radiation ranging from 5° to 85°. The Raman test of as-obtained materials was measured on a Raman Spectrometer attached LabRAM HR800 system (HORIBA, Korea) in the range of 1000 ~ 2000 cm^{-1}. Surface area measurements based on nitrogen adsorption isotherms were recorded using a surface properties analyzer instrument (ASAP 2020, Micromeritics). XPS was performed on a VG ESCALAB MK II X-ray photoelectron spectrometer. The analysis of element composition was conducted on energy dispersive X-ray spectroscopy (EDX, INCA x-sight, Oxford) and Elementar element analyzer (VARIO EI cube). The morphologies of the samples were verified using field-emission scanning
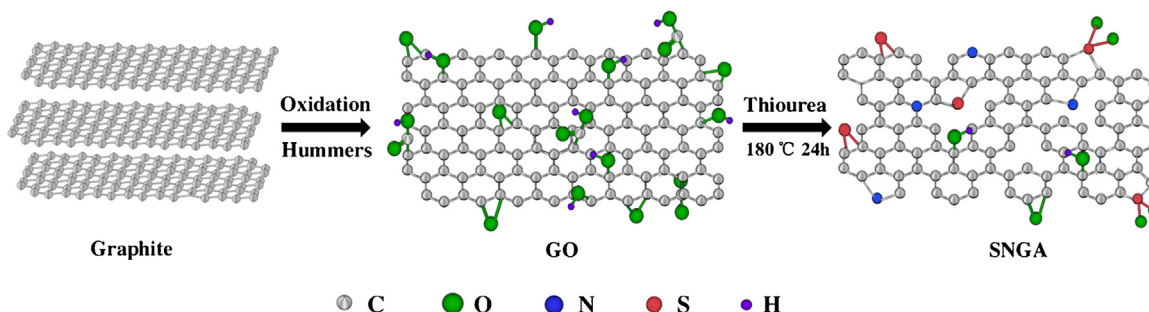
Scheme 1. Schematic design of S/N dual-doped GAs.