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A confined "microreactor" synthesis strategy to three dimensional nitrogen-doped graphene for high-performance sodium ion battery anodes

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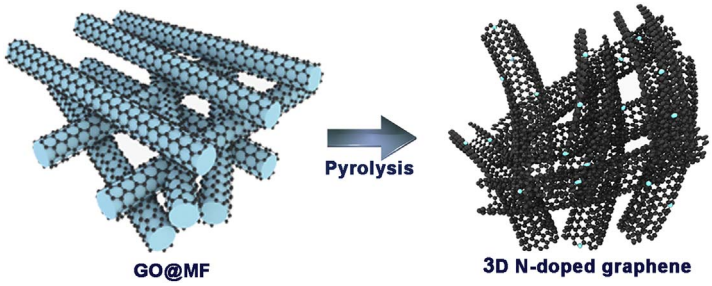
HIGHLIGHTS

- Designed a novel "microreactor" strategy for fabrication of 3D N-doped graphene.
- "Microreactor" was derived from a framework of melamine fibers wrapped by GO.
- "Microreactor" enhanced the conversion yield from melamine to N-doped graphene.
- The GO@MF-900 exhibited high capacity and superior cyclic capability for SIBs.

GRAPHICAL ABSTRACT



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ABSTRACT

In virtue of abundant sodium resources, sodium ion batteries (SIBs) have been regarded as one of the most promising alternatives for large-scale energy storage applications. However, the absence of a suitable anode material makes it difficult to realize these applications. Here, we demonstrate an effective synthesis strategy of using a "microreactor" consisting of melamine fiber (inside) and graphene oxide (GO, outside) to fabricate three dimensional (3D) nitrogen doped (N-doped) graphene as high-performance anode materials for sodium ion batteries. Through a controlled pyrolysis, the inside melamine fiber and the outside GO layer has been converted into N-doped graphene and reduced graphene oxide (*r*-GO) respectively, and thus the "microreactor" is transformed into interconnected 3D N-doped graphene structures. Such highly desired 3D graphene structures show reversible sodium storage capacities up to ~305 mA h g^{-1} after 500 cycles at a current density of 0.2 A g^{-1} and promising long cycling stability with a stable capacity of ~198 mA h g^{-1} at 5 A g^{-1} after 5000 cycles. The high capacity and superior durability in combination with the facile synthesis procedure of the 3D graphene structure make it a promising anode material for SIBs and other energy storage applications.

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1. Introduction

The rapid development of portable electronics and electric vehicles (EVs) has generated a huge demand for low-cost Li-ion batteries (LIBs) with increased energy density and cyclic stability [1–6]. Due to potential safety issues and a gradually increasing lithium price, sodium-ion batteries (SIBs), as a promising alternative to LIBs, have gradually attracted increasing attention due to the large abundance and wide availability (~2.3 wt% of Na in contrast with 0.0017 wt% of Li in the Earth's crust) and low cost (~$140 per ton) of sodium. Therefore, SIBs are expected to reduce the heavy reliance on LIBs and realize high-efficiency, sustainable, and cost-effective energy storage [7–11].

In recent years, significant research has been devoted to the development of high-performance anode materials for SIBs, and various carbonaceous materials including: hard carbon [12–14], carbon spheres [15,16], carbon fibers [17,18], and carbon nanotubes [19,20], have emerged as front runners besides the currently reported sodium transition metal oxides [21–24], sulfides [25–28], and Ti- and Sn-based compounds [29–32]. However, there are still two major challenges to be addressed. First, the ~55% increase in ionic radius of Na^+ ion as compared to Li^+ ion will cause a larger volume expansion upon intercalation [33,34]. Second, the insufficient kinetics of the Na^+ ion storage process in pristine-graphite restricts the rate capability [34]. To address these challenges, three-dimensional (3D) graphene structures, which not only possess the intrinsic properties of graphene, but also exhibit many advantages over graphene such as high specific surface area, low density, high mechanical strength, and excellent electrical conductivity, have been considered to play a significant role in energy storage and catalysis [35,36]. In the past several years, tremendous efforts have been devoted to developing synthetic strategies for 3D graphene structures with various morphologies and structures, including: template-assisted methods [37], self-assembly methods [38–40], and aerosolization [41]. For instance, Xu et al. demonstrated that 3D graphene formed by annealing freeze-dried GO foams could be used as the anode for SIBs, which showed superior electrochemical performance compared to reduced graphene [42]. Recently, Yan et al. reported reduced graphene oxide/carbon nanotubes (CNTs) sponge via freeze drying of graphene oxide/CNTs mixed solution combined with thermal treatment which had good rate performance and long life cycling performance when used as anodes for SIBs [43]. These approaches result in significant enhancement in the applications of 3D graphene for SIBs, making them competitive earth-abundant alternative electrode materials to the current oxides and sulfides.

However, these available methods still have some space for improvement (e.g. usually require complicated etching processes, and/or organic solvents) [44], and moreover, the factors that influence the electrochemical performance remain to be elucidated. Recent studies have shown that heteroatom (e.g., N, S, and P) doping is an effective way to improve the electrochemical performance of carbon materials by tuning the electronic and chemical properties [45,46]. Therefore, developing low-cost and large-scale synthesis methods to yield 3D graphene structures with both optimal nitrogen doping levels and porous structures are required to boost its application as high-performance SIBs anode materials. Recently, an *in situ* conversion from graphitic carbon nitride (g-C_3N_4) to nitrogen-doped graphene were demonstrated, providing the possibility of utilizing melamine as precursor to construct graphene structures [47], although the conversion efficiency remains to be improved. Inspired by this, to improve the conversion efficiency and build the 3D structure, a "microreactor" consisting of melamine fiber (inside, MF) with a coated protective GO layer (outside) has been applied in this work to achieve 3D nitrogen-doped (N-doped) graphene structures. After a controlled pyrolysis, the MF confined in the "microreactor" and coated GO layer will be converted into N-doped graphene and *r*-GO, respectively, with the formation of interconnected 3D N-doped graphene. The 3D N-doped graphene, as anode for SIBs, exhibits a high reversible capacity of ~305 mA h g^{-1} at a current density of 0.2 A g^{-1}after 500 cycles, and ultra-long cycle life with a stable capacity of ~198 mA h g^{-1} at 5 A g^{-1} after 5000 cycles. To our knowledge, utilizing a confined "microreactor" to construct 3D N-doped graphene structures has not yet been reported, which can further promote its actual application in the field of energy storage.

2. Experimental

2.1. Preparation of N-doped 3D graphene

In a typical reaction, 2.5 g melamine were dispersed into 100 mL ethylene glycol with ultrasonication for 30 min. Subsequently, 0.1 M nitric acid aqueous solution was immediately added into the melamine ethylene glycol solution under vigorous stirring until the pH value was reduced to 2.0 and the sol-gel consisting of MF was formed. 50.0 mg GO in ethylene glycol solution was added to the sol-gel solution, stirred for another 6 h, and then washed with ethanol three times. The GO@MF precursors were filtered, and dried at 70 °C for 12 h. Finally, the GO@MF-900 was obtained by heating the precursor to 320 °C (2 °C min^{-1}) for 2 h and further to 900 °C (5 °C min^{-1}) for another 2 h.

2.2. Characterization

The morphologies were recorded using a Hitachi SU8020 scanning electron microscope (SEM) and JEM−2100F (TEM and HRTEM). X−ray diffraction (XRD) measurements were performed on a Rigaku D/max 2500 diffractometer (Cu Kα radiation, λ = 0.15418 nm). Thermal gravimetric (TG) and differential scanning calorimetric (DSC) analyses were conducted on a SDT Q600 system at a heating rate of 5 °C min^{-1} under a 100 standard cubic centimeters per minute (sccm) Ar flow. Raman spectra were collected on a confocal Renishaw inVia Raman spectrometer using a 633 nm laser as the excitation source. FT-IR spectra were recorded on a PerkinElmer spectrometer in the range 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. X−ray photoelectron spectra (XPS) were recorded on an ESCALAB MKII system using Mg Kα as the excitation source. Brunauer–Emmett–Teller (BET) specific surface areas were measured by nitrogen adsorption–desorption analyses using a Micromeritics ASAP 2020 instrument.

3. Results and discussion

The as-designed "microreactor" strategy for the synthesis of 3DN-doped graphene structures is depicted in Fig. 1. As previously reported [48], melamine molecules can be assembled into fibers by π-π interaction and hydrogen bonding in ethylene glycol solution with diameters of ~100–540 nm and lengths of up to ~150–200 μm (Figs. S1 and S2). In this work, the functional groups (-OH and -COOH) on the surface of GO will bond with amine group (-NH_2) in melamine under acid conditions [49], and a self-assemble of MF will appear on the surface of GO. After a continuous stirring, the MF was wrapped by the GO (GO@MF). Then, 3D structures were achieved after a pyrolysis process. For clarity, the as-synthesized samples were labeled as GO@MF-*T*, where *T* denotes the pyrolysis temperature. In step I, the melamine was dissolved into ethylene glycol and MF could be formed with the pH value tuned to ~2.0 (Fig. 1a). Next, ~2 wt% GO (Fig. S3) was added into the MF solution under magnetic stirring for at least 6 h to ensure effective GO coverage on the MF surface (step II). Subsequently, a well-controlled two-step pyrolysis process (step III and IV) resulted in the formation of 3D N-doped graphene. Notably, the as-synthesized products of GO@MF-900 exhibited excellent structural stability and ultra-light characteristics (Fig. 1b–c).

As revealed by the SEM images (Fig. 2a–b and Fig. S4), one can clearly see that most of the MF were fully wrapped by GO sheets, while the diameter of the MF was increased to ~1.5 μm. To gain more information about the reaction process in the "microreactor", thermogravimetric (TG) measurements were carried out (Fig. 2c), which