



# 3D N-doped graphene nanomesh foam for long cycle life lithium-sulfur battery



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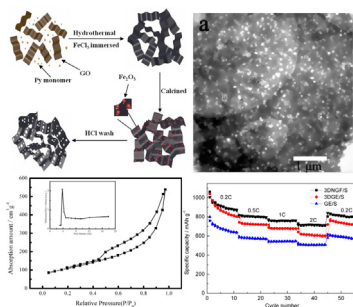
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## HIGHLIGHTS

- The nitrogen doping in graphene and etching graphene layers at the same time.
- The nanoholes on the graphene sheet have high density about  $1.4 \times 10^{10}$  holes per  $\text{cm}^2$ .
- The graphene still stable due to the nanoholes on graphene layers with not excessive damage of graphene lattice.
- The nanoholes on graphene layers help the electrolyte infiltrate into the electrode.

## GRAPHICAL ABSTRACT

The 3D N-doped graphene nanomesh foam (3DNGF) was synthesized by an in situ etching method. The nanoholes on the graphene sheets with diameter range approximately from 30 to 70 nm with high density about  $1.4 \times 10^{10}$  holes per  $\text{cm}^2$ . The specific surface area of 3DNGF is  $384 \text{ m}^2 \text{ g}^{-1}$ , much higher than the common 3D graphene. After 0.5C for 500 cycles, the 3DNGF/S exhibits a specific capacity of  $578 \text{ mAh g}^{-1}$  with a capacity decay only 0.06% per cycle. Even at 2C rate, the reversible specific capacity still was  $729 \text{ mAh g}^{-1}$ .



## ARTICLE INFO

### Article history:

Received 15 February 2017  
Received in revised form 24 May 2017  
Accepted 25 May 2017  
Available online 26 May 2017

### Keywords:

Lithium-sulfur  
Graphene  
N-doped  
Cycle performance

## ABSTRACT

The 3D N-doped graphene nanomesh foam (3DNGF) has been synthesized as the Lithium-sulfur battery cathode material for the first time. A method of in situ doping nitrogen and meanwhile etching graphene layer is introduced. The BET result shows the 3DNGF has a large specific surface area more than traditional three-dimensional graphene. Transmission electron microscopy (TEM) observation and Raman spectra confirm the nanoholes on the graphene. The 3DNGF/S composite exhibits an initial discharge capacity of  $1134 \text{ mAh g}^{-1}$  at 0.2C in the first cycle with the sulfur utilization of 67%. The electrode reserves a specific capacity of  $578 \text{ mAh g}^{-1}$  after 500 cycles at 0.5C, with a capacity decay of 0.06% per cycle. Its specific capacity at 2C can still reach to  $729 \text{ mAh g}^{-1}$ , indicating the good rate performance.

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## 1. Introduction

As the ever-growing demand in power sources for advanced electric devices, Lithium-sulfur (Li-S) batteries with high

theoretical specific capacity ( $1672 \text{ mAh g}^{-1}$ ) and energy density ( $2600 \text{ Wh kg}^{-1}$ ) have been recently considered as a promising successor to Lithium-ion batteries (LIBs) [1,2]. Although the notion of Li-S batteries is raised in the 1960s [3], their large-scale applications have been long hindered by three main problems: (i) the poor rate performance is due to insulating characteristics of sulfur and lithium sulfides ( $\text{Li}_2\text{S}$  and  $\text{Li}_2\text{S}_2$ ) [4]; (ii) the fast capacity fading is

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due to the migration of  $\text{Li}_2\text{S}_n$  to the anode and deposition of some species on the anode [5]; (iii) the structural failure is due to the volume expansion of discharge product [6].

Many efforts have been devoted to promote the practical applications of the Li-S battery, such as synthesizing the novel composite cathode materials [7–9]; placing functional interlayers [10,11]; protecting the lithium metal anode [12,13]. Among these efforts, the synthesis of the novel composite cathode materials is the focus of study [14,15]. In order to improve the electrical conductivity, scholars have tried to synthesize cathode materials use carbon-based materials [16,17], polymer [18,19] and metal oxide [20,21]. Carbon-based materials with good conductivity and chemical stability, making them the most promising hosts for sulfur in Li-S batteries. Since been discovered in 2004 [22], graphene has attracted increasing attention because of its unique two-dimensional structure [23], high surface area [24,25] and excellent chemical stability. Zhou et al. [26] prepared the sulfur@polypyrrole/graphene cathode material use  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  as the reducing agent which is dangerous. After 200 cycles at 0.2C, the capacity loss is 51%. Even at a low rate of 1C, the reversible capacity is only  $566 \text{ mAh g}^{-1}$ . Constituted by 2D graphene sheets, 3D graphene with faster electron and mass transport due to the three-dimensional crosslinking structure [27,28]. In Lithium-sulfur batteries, 3D graphene applied in cathode material has been deeply researched [29]. Xu et al. [30] prepared three-dimensional graphene as sulfur host for cathode materials. After 100 cycles at 0.2C, the capacity retention is less than 56%. Only a reversible capacity of  $500 \text{ mAh g}^{-1}$  at 2C shows the weak rate performance. Therefore, the application of 3D graphene in Lithium-Sulfur battery need further research.

Recently, doping nitrogen atom into the graphene layers has been proved to be an effective access to improve the electrochemical properties [31,32]. The 3D porous structure provides large surface area for the distribution of sulfur [33]. At the same time, the adequate space for the volume expansion of discharge product which protect the cathode structure [14]. Nitrogen atom in graphene not only contributes to fast transport of electrons and lithium ions, but also chemical bonding polysulfides [34,35]. Note that the contact of electrolyte and sulfur inside the electrode is not very well due to the block of complete graphene layer. Though with the nitrogen doped, the rate performance in the graphene with three dimensional structure is still not ideal. The specific surface area of 3D graphene prepared by hydrothermal treatment is still smaller than most of the carbon materials [36,37]. Designing graphene-based materials with nitrogen doping and porous structure on the graphene sheet is a feasible way (Table S2).

In this work, we introduce a 3D N-doped graphene nanomesh foam (3DNGF) as the host of sulfur. The nitrogen-doping process was carried out by calcining the polypyrrole. At the same time, the nano holes on graphene layers were produced by calcining the  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$  nanoparticles. The 3DNGF with a hierarchically mesoporous structure facilitates the physical adsorption polysulfide and the inside sulfur utilization. The nitrogen atom doped in graphene enhances the electronegativity of the sheet surface and chemical absorbing efficiency of polysulfide.

## 2. Experimental

### 2.1. Synthesis of graphene (GE) and 3D-graphene (3DGE)

Graphene oxide (GO) was prepared by a modified Hummers method. Typically, 5.0 g graphite powder was added into 180 mL concentrated  $\text{H}_2\text{SO}_4$  and 60 mL fuming  $\text{HNO}_3$ . After cooling down to room temperature, 25 g  $\text{KMnO}_4$  was slowly added to the mixture. 600 mL deionized water and 30 mL  $\text{H}_2\text{O}_2$  were slowly added after 120 h. The slurry was centrifuged and washed with deionized

water until the pH of the slurry is neutral. The remaining yellow solid was freeze-dried overnight. GE was prepared by heating the GO at  $850^\circ\text{C}$  for 2 h under Ar atmosphere. The heating speed was  $5^\circ\text{C min}^{-1}$ . To synthesis of the 3DGE, 30 mL homogeneous GO aqueous ( $2 \text{ mg mL}^{-1}$ ) dispersion was sealed in a 50 mL Teflon-lined autoclave and maintained at  $180^\circ\text{C}$  for 12 h. Then the autoclave was naturally cooled to room temperature, the prepared gel was taken out and freeze-dried overnight.

### 2.2. Synthesis of 3D N-doped graphene nanomesh foam (3DNGF)

First of all, 0.9 mL of pyrrole (Py) was added into 30 mL homogeneous GO aqueous ( $2 \text{ mg mL}^{-1}$ ). After vigorous stirring for 10 min, the mixture was sealed in a 50 mL Teflon-lined autoclave and maintained at  $180^\circ\text{C}$  for 12 h. After the autoclave was naturally cooled to room temperature, the prepared gel was taken out and immersed into 0.3 M  $\text{FeCl}_3$  solution. After freeze-drying, the gel was heating at  $850^\circ\text{C}$  for 2 h under Ar atmosphere with a heating speed of  $5^\circ\text{C min}^{-1}$ . The 3DNGF was obtained by washing the gel with HCl and deionized water and freeze-drying.

### 2.3. Characterization

The XRD was conducted with a Bruker D8 ADVANCE. Thermogravimetric analysis was performed with a TG 209 F3 Tarsus in nitrogen with a heating speed of  $5^\circ\text{C min}^{-1}$  to  $450^\circ\text{C}$ . The SEM was performed by Hitachi SU70. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were performed using a TECNAI G2 F30 field emission transmission electron microscope. The BET data were obtained by QUADRASORB SI Automated Surface Area&Pore Size Analyzer. The Raman spectroscopy was tested by Renishaw inVia Raman Microscope. X-ray photoelectron spectroscopy (XPS) analysis was carried out with a physical electronics PHI model 5600 instrument. The Al X-ray source was operated at 250 W and the take-off angle of the sample to analyzer was  $45^\circ$ . Survey spectra were collected at pass energy (PE) of 187.85 eV over a binding energy range from 0 eV to 1300 eV. High binding energy resolution multiplex data for the individual elements were collected at a PE of 29.55 eV. During all XPS experiments, the pressure inside the vacuum system was maintained at  $1 \times 10^{-9}$  Pa. Before the analysis above, all the samples were dried under vacuum at  $80^\circ\text{C}$  overnight. The curves fitting are use PC-ACCESS software. The peak positions are based on the previous work [38,39].

### 2.4. Electrochemistry tests

The 3DNGF/S was prepared via a facile melt-diffusion strategy at  $155^\circ\text{C}$  for 12 h by the previous articles [40]. The electrochemical performance of 3DNGF/S composite was evaluated using CR2025 coin-type cells assembled in an argon-filled glove box ( $\text{O}_2 < 0.1 \text{ ppm}$ ;  $\text{H}_2\text{O} < 0.1 \text{ ppm}$ ). The 3DNGF/S composite was mixed with PVDF (poly-vinylidene-fluoride) and Super-P in a weight ratio of 8:1:1, with NMP (N-2-methyl pyrrolidone) as a dispersant. The slurry was coated on carbon-coated aluminum foil and dried in a vacuum at  $60^\circ\text{C}$  overnight. The carbon-coated aluminum foil has no influence on the electrochemical properties (Fig. S1c). The active material loading was about  $1 \text{ mg cm}^{-2}$ . The electrolyte was  $1.0 \text{ mol L}^{-1}$  LiTFSI (lithium bis(trifluoromethanesulfonyl)imide) and  $0.1 \text{ mol L}^{-1}$   $\text{LiNO}_3$  in a mixture of DOL (dioxolane) DME (1,2-dimethoxyethane). Galvanostatic charge/discharge tests were performed between 1.7 and 2.5 V to evaluate the capacity and cycle performance of three electrodes. The electrochemical impedance spectroscopy (EIS) measurement was conducted at open-circuit condition with a frequency range from  $2.0 \times 10^6 \text{ Hz}$  to  $1.0 \times 10^{-2} \text{ Hz}$  with CHI650E electrochemical work station.

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