



# Simultaneous optimization of surface chemistry and pore morphology of 3D graphene-sulfur cathode via multi-ion modulation



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## HIGHLIGHTS

- 3D porous NSG is synthesized under ammonia and sulfide ion modulation.
- The surface chemistry and pore morphology of NSG is simultaneously optimized.
- The S@NSG cathode exhibits long cycle life and high capacity.

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## ABSTRACT

Lithium/sulfur (Li/S) battery is a promising next-generation energy storage system owing to its high theoretical energy density. However, for practical use there remains some key problems to be solved, such as low active material utilization and rapid capacity fading, especially at high areal sulfur loadings. Here, we report a facile one-pot method to prepare porous three-dimensional nitrogen, sulfur-codoped graphene through hydrothermal reduction of graphene oxide with multi-ion mixture modulation. We show solid evidence that the results of multi-ion mixture modulation can not only improve the surface affinity of the nanocarbons to polysulfides, but also alter their assembling manner and render the resultant 3D network a more favorable pore morphology for accommodating and confining sulfur. It also had an excellent rate performance and cycling stability, showing an initial capacity of 1304 mA h g<sup>-1</sup> at 0.05C, 613 mA h g<sup>-1</sup> at 5C and maintaining a reversible capacity of 462 mA h g<sup>-1</sup> after 1500 cycles at 2C with capacity fading as low as 0.028% per cycle. Moreover, a high areal capacity of 5.1 mA h cm<sup>-2</sup> at 0.2C is achieved at an areal sulfur loading of 6.3 mg cm<sup>-2</sup>, which are the best values reported so far for dual-doped sulfur cathodes.

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## 1. Introduction

Nowadays, the rapidly growing demand of the emerging markets of electric vehicles and grid energy storage have made the development of advanced energy storage technologies a global

imperative [1–3]. Among them, lithium/sulfur (Li/S) batteries have attracted much attention due to their great potential to become next-generation mainstream energy storage systems because of their ultra-high theoretical specific capacity of 1675 mA h g<sup>-1</sup> and theoretical energy density of 2600 Wh kg<sup>-1</sup>, which far exceeds those of employing active materials in state-of-the-art lithium-ion batteries. However, the poor cycling performance caused by the sulfur's insulating nature, the large volumetric expansion (~80%) and the high-solubility of the intermediate polysulfides in ether-based electrolytes is still one of the biggest challenges for Li/S cells that has hindered Li/S batteries' commercialization [4–7]. To be comparable to state-of-the-art Li-ion batteries and match the energy requirements for transportation, the areal specific capacity

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of Li/S cells needs to be in the range of 3–7 mA h cm<sup>-2</sup>, corresponding to a sulfur loading of at least 3–7 mg cm<sup>-2</sup> [8–10]. It becomes even more challenging to solve the above problems at such high sulfur loadings. Therefore, the efforts in searching for efficient sulfur immobilizers have never been exhausted to suppress the dissolution of high-order polysulfides and improve the cell's cycle life.

Incorporation of sulfur into a porous conductive matrix has been proved to be an effective way to improve the sulfur utilization and prolong the cell's cycle life [11–13]. An ideal matrix should be able to conduct electrons efficiently to/from the insulating active phase, confine elemental sulfur and the insoluble discharged products (Li<sub>2</sub>S<sub>2</sub> and Li<sub>2</sub>S) in nanoscale or even smaller dimensions, and trap polysulfides against dissolution loss while still maintaining effective channels for electrolyte infiltration and lithium (Li) ion transportation. Regarding the pore size, efficient Li ion transport and strong confinement of sulfur and polysulfides are often two trade-off features of a matrix, since smaller pores are more favorable for trapping the sulfur species while bigger pores are preferred to ensure good electrolyte accessibility and high Li ion mobility [11,14–16]. Therefore, it is of great importance to combine small pores (micropores and small mesopores) with large pores (big mesopores and macropores) in a rational way in the same matrix [17]. Furthermore, to ensure a high mass loading of sulfur and to accommodate the large volumetric change of the active phase during lithiation, the matrix material should possess a specific pore volume as great as possible on the premise of a sufficient robustness [8,18]. Over the years, extensive efforts have been made on developing various nanostructured carbon-based matrices such as ordered porous carbons [8,19], carbon nanotubes and nanofibers [20,21], graphene and heteroatom doped graphene [22–24], carbon nanotube/graphene hybrids [25,26], and so on. Among these materials, 3D graphene, a three-dimensional macroscopic architecture assembled from 2D flexible graphene nanosheets, has gained great attention due to its highly porous structure, good electrical conductivity, and outstanding mechanical properties [27,28]. While all the 3D graphene materials applied to fabricate sulfur cathodes in the literature are characteristic of a hierarchical pore structure, a fine tuning and optimization of the pore morphology is yet to be done. Previous studies on other porous carbon materials have explicated the crucial role of small mesopores (2–10 nm) in improving carbon-sulfur interaction, trapping of polysulfides, and serving as interconnectors between larger pores for fast Li ion transport. While the macropores and large mesopores in 3D graphene can be readily tuned by changing the concentration of graphene in suspension prior to self-assembly, micropores and small mesopores are generally introduced by using etchable nanoparticles/nanospheres as templates [11,14,19,29–31]. The template methods are of good controllability but suffer from high complexity. Therefore, it is highly desirable to develop a simple and cost-effective way to increase the amount of small mesopores in 3D graphene assemblies.

Besides of tailoring the topological structure for physical confinement of polysulfides, chemical doping/functionalization of the carbon surfaces (pore walls) has been proved as another effective way to improve the matrix-sulfur interactions [32,33]. Carbon matrices doped by heteroatoms such as O, N, S, and B have achieved significant success in improving the cycling stability and Coulombic efficiency of sulfur cathodes [23,24,34]. These heteroatomic groups could help to attract the polysulfides through chemical binding (e.g. N ... Li<sub>2</sub>S<sub>x</sub> complexation for N containing groups) and prevent the random deposition and agglomeration of the insoluble polar products (Li<sub>2</sub>S<sub>2</sub> and Li<sub>2</sub>S). Meanwhile, they would not significantly impact the diffusion rate of lithium ions [35,36]. Recently, dually doped nanocarbons have aroused special

interests as sulfur hosts for advanced Li/S batteries. Nazar's group synthesized N,S dual-doped mesoporous carbon using a template method and derived high-performance Li/S cells from it [30]. The greatly improved interaction of the dual-doped carbon with lithium polysulfides have been confirmed both experimentally and theoretically. Manthiram and coworkers explored N,S codoped graphene sponge in combination with Li<sub>2</sub>S<sub>6</sub> catholyte to build a type of free-standing 3D cathodes with high active material loadings and significantly improved energy density and cycling stability [18]. The authors indicated the merits of the macropores (2–8 μm) in such a structure while paid little attention to the small mesopores. In the present work, we have developed a novel facile method to synthesize N,S-codoped 3D porous graphene through hydrothermal reduction of graphene oxide (GO) with multi-ion mixture modulation. We found that the 3D architecture assembled from the graphene treated by two ions modulation got much more small mesopores than that assembled from the only one counterparts. Note that our 3D sponges were obtained in a large volume scale at a substantially low concentration of the GO precursor, suggesting that there exist strong non-stacking interactions by multi-ion modulation among the N,S-codoped nanosheets so that the assembly is of both high stability and high porosity. From a practical viewpoint, our strategy is very meaningful since it improves the surface chemistry and the pore morphology of the conductive matrix simultaneously by a single step one-pot synthesis via multi-ion modulation. More importantly, the so-built 3D framework enables high areal sulfur loadings due to the rationalized arrangement of pores of different sizes.

## 2. Experimental section

### 2.1. Preparation of graphene oxide (GO)

The graphene oxide was synthesized by an improved Hummer's method [31]. Firstly, the pre-oxidized graphite powder (0.5 g) was put into concentrated H<sub>2</sub>SO<sub>4</sub> (12 mL), followed by gradually adding KMnO<sub>4</sub> (1.5 g) under vigorous stirring in the ice water bath. Secondly, the mixture was stirred at 35 °C for 2 h, and then diluted with deionized (DI) water (24 mL). Thirdly, the resultant mixture was stirred at an elevated temperature of 98 °C for 0.5 h. After cooling to room temperature, an additional 70 mL DI water was added, and shortly, 1.25 mL 30% H<sub>2</sub>O<sub>2</sub> was added. Finally, the mixture was washed by 5 wt% HCl aqueous solution (125 mL) to remove metal ions, followed by washing with DI water three times and centrifugation. Dialysis was carried out to further remove the remaining metal species.

### 2.2. Preparation of heteroatom-doped graphene

100 mL GO stock solution (4 mg mL<sup>-1</sup>) was diluted with 300 mL ultrapure DI water. The dilution was firstly sonicated for 1 h, and then 800 mg of sodium sulfide and 2 mL of ammonia were added. The mixed solution was transferred into a 100 mL Teflon liner, stainless steel autoclaved and placed in an oven at 180 °C for 8 h. The resultant solid product was collected by filtration, washed with water and alcohol, and freezing dried for 24 h to yield nitrogen and sulfur-codoped graphene (NSG). The sulfur-doped graphene (SG), nitrogen-doped graphene (NG), and reduced graphene oxide (RGO) were synthesized by the same method, with sodium sulfide but without ammonia, with ammonia but without sodium sulfide, and in the absence of both of them, respectively.

### 2.3. Preparation of heteroatom-doped graphene-sulfur composites

0.72 g elemental sulfur was added to a sodium sulfide solution

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