



## Improving the performance of lithium–sulfur batteries by graphene coating



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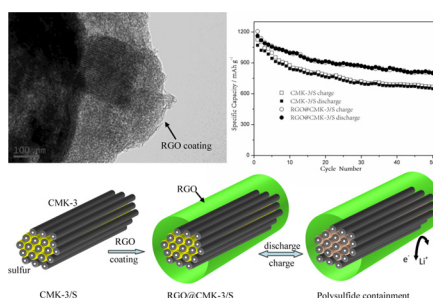
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### HIGHLIGHTS

- A novel approach for solving the capacity loss in mesoporous carbon/sulfur material.
- A hybrid structure by incorporating the merits of CMK-3 matrix and graphene skin.
- Graphene-coated mesoporous carbon/sulfur composite was synthesized.
- The RGO@CMK-3/S composite cathode exhibits improved electrochemical properties.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A graphene coating mesoporous carbon/sulfur (RGO@CMK-3/S) composite, which is characteristic of a hybrid structure by incorporating the merits of CMK-3 matrix and graphene (RGO) skin, is synthesized by a facile and scalable route. The CMK-3/S composite is synthesized *via* a simple melt-diffusion strategy, and then a thin RGO skin is absorbed on the CMK-3/S composite surface in aqueous solution. When evaluating the electrochemical properties of as-prepared RGO wrapped nanostructures as cathode materials in lithium–sulfur batteries, it exhibits much improved cyclical stability and high rate performance. The RGO@CMK-3/S composite with 53.14 wt.% sulfur presents a reversible discharge capacity of about 734 mA h g<sup>-1</sup> after 100 cycles at 0.5 C. The improved performance is attributed to the unique structure of RGO@CMK-3/S composite. CMK-3 with extensively mesopores can offer buffering space for the volume change of sulfur and efficient diffusion channel for lithium ions during the charge/discharge process. Meanwhile, the conductive RGO coating skin physically and chemically prevents the dissolution of polysulfides from the cathode, both of which contribute to the reduced capacity fade and improved electrochemical properties.

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### 1. Introduction

Recently, with the rapid development of portable electronic equipment, electric vehicles and intelligent power grid and other areas, a higher demand for batteries with high power and energy density and longer cycling life has been put forward, and developing a new generation of battery system is becoming more and

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more urgent [1,2]. Lithium–sulfur batteries, due to its numerous appealing characteristics such as high theoretical specific capacity ( $1675 \text{ mA h g}^{-1}$ , based on the complete reactions of sulfur with lithium metal to form  $\text{Li}_2\text{S}$ ), high theoretical specific energy ( $2500 \text{ Wh kg}^{-1}$ , with a Li electrode), environmental benignity, abundant and cheap sulfur resources, have attracted tremendous attention and are very promising to be the next generation of high energy density lithium batteries [3–5].

However, before the full utilization of sulfur as a practical cathode material, there are still a number of issues needed to be addressed. Firstly, sulfur has a low intrinsic conductivity ( $5 \times 10^{-30} \text{ S cm}^{-1}$  at  $25^\circ\text{C}$ ) [4]. Secondly, the dissolution of long chain polysulfides anions ( $\text{S}_n^{2-}$ ) that are generated during the charge/discharge process is the main problem [5]. Dissolved polysulfides can transfer to the lithium anode where they are reduced to form insoluble precipitates, such as  $\text{Li}_2\text{S}$  or  $\text{Li}_2\text{S}_2$ , which cause the fading of active materials. These disadvantages lead to low utilization of sulfur active material, low coulombic efficiency and rapid capacity loss during cycling [6,7]. Enormous efforts have been demonstrated to overcome the insulating property of sulfur and prevent the dissolution of polysulfides by developing novel electrolyte [8–10], embedding sulfur in nano-pores and micro-pores of active carbon [6,7,11–13], carbon nanotubes [14–17], graphene [18–21] and conductive polymer matrix [22–24]. With these strategies, the polysulfides can be trapped to some extent in the additive materials which have a large surface area and a high porous structure. Among these efforts, mesoporous carbon is a very attractive material, because of their small pore size and larger overall pore volume, incorporating sulfur into mesoporous carbon structures can contain the polysulfides to some extent during the charge/discharge process [6,11]. However, sulfur in the mesopores could still be accessed by the electrolyte in which polysulfides could be dissolved, the active material loss could only be alleviated, but not eliminated. Thus, it is essential to design novel approaches for solving the specific capacity loss caused by the dissolution of polysulfides in mesoporous carbon/sulfur composite.

Recently, several studies have shown that a high electrochemical performance nanocarbon/sulfur electrode can be achieved by designing a building block into nanocarbon/sulfur materials to form a hybrid nanostructure, such as PEG/ mesoporous carbon hybrid nanostructure [3], PEG/graphene hybrid nanostructure [19], graphene/carbon nanotubes hybrid nanostructure [25] and PEG/ carbon nanotubes hybrid nanostructure [26]. Forming hybrid structures with highly conductive carbons materials is one of the most promising methods to improve the electrochemical performance of sulfur cathodes. In addition, Graphene (or reduced graphene oxide), as a two-dimensional nanomaterial with high surface area of over  $2600 \text{ m}^2 \text{ g}^{-1}$ , excellent conductivity, superior structural flexibility and mechanical strength, has been considered a viable nanocarbon component for the advanced lithium–sulfur batteries cathode electrodes [18–21,27–31]. Especially, the reduced graphene oxide which was functionalized with various groups, such as hydroxyl and carboxyl groups, could interact strongly with polysulfides to accomplish better trapping and achieve superior cycling performances [20,28]. In this work, we present a facile and scalable route to fabricate graphene-coated mesoporous carbon/sulfur composite. Active sulfur particles were highly dispersed in the channels and maintained intimate contact with the mesoporous carbon. Mesoporous carbon can offer the necessary buffering space for volume change of sulfur and efficient diffusion channel for lithium ions during the charge/discharge process as well, which acts as “micro-reactors” for the electrochemical reaction. The conductive graphene (RGO) skin coated on the surface of mesoporous carbon can trap soluble polysulfides intermediates, which can further alleviate the polysulfides shuttle [27–31]. As a

result, the graphene-coated mesoporous carbon/sulfur composite shows a notably improved electrochemical performance.

## 2. Experimental

### 2.1. Material synthesis and characterization

#### 2.1.1. Preparation of CMK-3 and CMK-3/S composite.

The CMK-3 mesoporous carbon was synthesized as described in Nazar's paper [3]. 1.25 g glucose was dissolved in 5.0 mL of deionized water with 0.14 g  $\text{H}_2\text{SO}_4$ . 1.0 g SBA-15 (99% purity, 8 nm, 400–600  $\text{m}^2/\text{g}$ , XF Nano, Co. Ltd, China) mesoporous silica was dispersed and sonicated in the above solution. Then the mixture was heated at  $100^\circ\text{C}$  for 12 h, followed by another 12 h at  $160^\circ\text{C}$ . This impregnation process was then repeated with another 5.0 ml aqueous solution containing 0.8 g glucose and 0.09 g  $\text{H}_2\text{SO}_4$ . Finally, the composite was carbonized at  $900^\circ\text{C}$  for 3 h in an argon atmosphere, and SBA-15 silica template was removed by 5 wt.% HF solution at room temperature for 4 h.

The CMK-3/S composites were then prepared, in a sealed Teflon container for 12 h at  $155^\circ\text{C}$ , followed by another 2 h at  $300^\circ\text{C}$  under argon condition, by simply heating pre-mixed sublimed sulfur and corresponding carbon at an accurate weight ratio of 60:40. The prepared CMK-3/S composites were dispersed in 200 mL aqueous solution in which 0.2 ml of 1 wt.% Triton X-100 (a surfactant with a PEG chain) aqueous solution was added.

#### 2.1.2. Preparation of RGO@CMK-3/S composite

Graphene oxide (GO) was synthesized by oxidation of graphite using improved Hummers' method as reported elsewhere [32]. A certain amount of GO aqueous suspension ( $10.0 \text{ mg mL}^{-1}$ ) was diluted to  $1.0 \text{ mg mL}^{-1}$  with distilled water. The dispersed CMK-3/S aqueous solution was then added into the GO aqueous suspension and the mixture was sonicated for 1 h to achieve a black homogeneous aqueous suspension. A certain amount of hydrazine hydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ) was subsequently added to reduce graphene oxide to graphene. After stirring for 12 h at room temperature, the RGO@CMK-3/S composites were collected by consecutive centrifugation and water-washing cycles as well as lyophilization.

Characterization of CMK-3, CMK-3/S composite and RGO@CMK-3/S composite were carried out by scanning electron microscopy (SEM, JSM-6360LV, Japan), transmission electron microscopy (TEM, JEM-2100F, Japan) and X-ray diffraction (XRD, Rigaku-TTRIII, Japan).

### 2.2. Electrochemical measurements

The electrode consisted of 80 wt.% the as-prepared RGO@CMK-3/S composite, 10 wt.% polyvinylidene fluoride (PVDF) binder and 10 wt.% conductive carbon black. To form the sulfur electrode, the materials were mixed, dispersed in N-methyl-2-pyrrolidinone (NMP), and coated on an aluminum foil. After drying at  $60^\circ\text{C}$  for 24 h, the electrodes were incorporated into 2025 coin-type cells in a glove box filled with Ar gas, using lithium metal ( $\Phi = 1.54 \text{ cm}$ ) as the counter electrode, 1 M bis(trifluoromethanesulfonyl)imide lithium (LiTFSI, Sigma–Aldrich) and 0.1 M  $\text{LiNO}_3$  (Aladdin) in a mixture solution of dimethoxyethane (DME, Aldrich Co.) and 1,3-dioxolane (DOL, Aldrich Co.) (volume rate 1:1) as the electrolyte, and polyethylene film as the separator. The 2025 coin-type cells were galvanostatically cycled on a LAND CT2001A instrument (Wuhan, China) at room temperature. The cutoff potentials for charge and discharge were set at 2.8 V and 1.7 V vs.  $\text{Li}^+/\text{Li}$ , respectively. Specific capacity was corrected based on the mass of sulfur, and a typical sulfur mass loading on the electrode was  $0.7\text{--}0.8 \text{ mg cm}^{-2}$ . In this study, 1 C corresponds to a current density value of  $1680 \text{ mA h g}^{-1}\text{-sulfur}$ . Cyclic voltammograms (CV)

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