



# Preparation of three-dimensional hybrid nanostructure-encapsulated sulfur cathode for high-rate lithium sulfur batteries



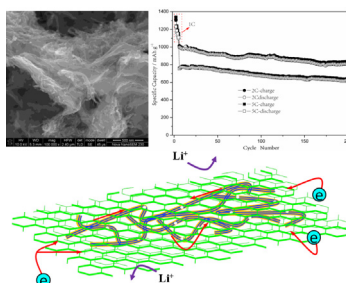
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## HIGHLIGHTS

- A novel approach for high-rate lithium sulfur batteries.
- A three-dimensional hybrid structure by incorporating the merits of MWCNTs and graphene.
- The RGO@MWCNTs-W/S composite cathode exhibits an admirable high-rate performance.
- This work makes much sense to the structure designing of novel sulfur-based materials.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A three-dimensional hybrid nanostructure incorporating the merits of the MWCNTs webs (MWCNTs-W) and the reduced graphene oxide (RGO) is designed to improve the high-rate cycling performance of the lithium-sulfur batteries. Owing to the excellent  $\text{Li}^+$  ion and electronic transport properties of the MWCNTs-W and the RGO, this unique structure can provide a three-dimensional conductive network and promote rapid charge-transfer reaction at the cathode. Furthermore, because of the rough surface and porous structure of the MWCNTs after activation with KOH, and the special adsorption ability of the RGO, the soluble polysulfide intermediates can be effectively trapped in the cathode. Therefore, when evaluating the electrochemical properties of the RGO@MWCNTs-W/S composite as the cathode material for lithium-sulfur batteries, it exhibits an excellent cyclical stability and high rate performance. In particular, even at an ultrahigh rate (5 C), a discharge capacity as high as  $620 \text{ mAh g}^{-1}$  is still retained for the RGO@MWCNTs-W/S composite with 68.93 wt% sulfur after 200 cycles, and the average coulombic efficiency is 96%.

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## 1. Introduction

As the key electrical energy storage devices for portable electronics and power tools, rechargeable lithium ion batteries have achieved great development during the past decades [1,2]. However, the commercialized lithium ion batteries will become

insufficient for the future electric vehicles due to the low capacity of conventional cathode materials (for example,  $\sim 150 \text{ mAh g}^{-1}$  for layered oxides and  $\sim 170 \text{ mAh g}^{-1}$  for  $\text{LiFePO}_4$ ) [3,4]. Developing novel electrode materials with higher gravimetric and volumetric capacities is becoming increasingly urgent. Sulfur, as one of the most abundant elements on the earth, can react with metallic lithium to form  $\text{Li}_2\text{S}$  by a two-electron reaction, and offers a high theoretical capacity of  $1675 \text{ mAh g}^{-1}$  and a high theoretical energy density of  $2600 \text{ Wh kg}^{-1}$ , making it a potential high capacity cathode material for the next rechargeable batteries [5].

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However, due to some major problems, commercial applications of lithium sulfur batteries have not been very successful even after several decades of research. Such major problems include the insulating nature of sulfur ( $5 \times 10^{-30} \text{ S cm}^{-1}$  at  $25 \text{ }^\circ\text{C}$ ) and its reduced products, leading to low utilization of active material [6]. In addition, the high solubility of polysulfide intermediates in the electrolyte and the shuttle of the high-order polysulfides ( $\text{Li}_2\text{S}_x$ ,  $2 < x \leq 8$ ) between the electrodes during cycling both result in loss of active material and low coulombic efficiency [5]. Moreover, sulfur cathodes undergo significant volume expansion and contraction during charge and discharge. This volume change ( $\sim 80\%$  for sulfur) can result in pulverization of the initial particle morphology and cause the loss of electrical contact between active materials and the cathode framework [4,7].

In recent years, various strategies including the optimization of the organic electrolyte or additives [8–12], the application of protective films for the lithium anode [13,14], the fabrication of sulfur/conductive polymer composites [15–18] and sulfur/carbon composites [2–4,6,7,19–33], were developed to improve the electrochemical performance of sulfur cathodes. Among the strategies, encapsulating sulfur in the porous carbon materials (such as ordered mesoporous and microporous carbon [2,4,19–24], carbon nanotubes [25–31], porous fibers [4,7,29,32] et al.), which can minimize or avoid the shuttle of polysulfides because of their large surface area, high porous structure and strong adsorption ability, has been demonstrated to be one of the most highly desired methods to improve the cycle life of lithium-sulfur batteries.

While, owing to the inevitable dissolution of the polysulfides into the electrolyte through the channels of the porous carbon, especially at high rates, achieving a high capacity and cycling performance for sulfur/carbon cathode under high-rate conditions remains a challenge [21]. It is noted that the multi-walled carbon nanotubes (MWCNTs) are an attractive choice as the carbon matrix and electric conductor for high-rate sulfur cathodes due to their excellent electrical and unique structure. Because of their high aspect ratio, MWCNTs can provide faster  $\text{Li}^+$  diffusion pathways, which will contribute to improve the rate performance of the sulfur

cathode [26,28,30]. However, on account of the low surface areas and limited pore volumes, amount of sulfur would be crystallized on the outer surface of the MWCNTs, which would easily dissolve into the electrolyte and lead to the capacity fading. However, if the closed ends of the MWCNTs were opened and much more pores on the walls were created, the sulfur would be incorporated into the channels of the MWCNTs and the diffusion of polysulfides would be further minimized. Fortunately, the above assumption has been achieved by activation of the MWCNTs with KOH [33–35]. Moreover, according to the recent studies and our previous work, forming hybrid structure with highly conductive carbon material, such as PEG/mesoporous carbon hybrid nanostructure [2], graphene@CMK-3 hybrid nanostructure [36], PEG/graphene hybrid nanostructure [37], graphene/CNTs hybrid nanostructure [38] and PPy/PEG-modified CNTs hybrid nanostructure [39], is another promising method to further improve the electrochemical performance of the sulfur cathodes. In this work, we developed a three-dimensional hybrid nanostructure by incorporating the merits of the MWCNTs and the RGO to improve the high-rate cycling performance of the lithium-sulfur batteries (Fig. 1 shows the schematic diagram of the steps for synthesizing the hybrid nanostructure). First, activation of MWCNTs with KOH at high temperature was employed to obtain porous MWCNTs and achieve a MWCNTs webs structure (MWCNTs-W). Next, sulfur was incorporated into MWCNTs-W via a simple melt-diffusion method. Then the MWCNTs-W/S composites were pre-modified by the cationic surfactant (SDS) to carry up positive charge. Finally, the GO nanosheets with abundant negatively charged surface functional groups were conducted to self-assemble on the surface of the MWCNTs-W/S composites by electrostatic attraction [40]. In addition to the excellent adsorption ability of RGO and MWCNTs-W in trapping soluble polysulfides intermediates, both of them can also provide fast  $\text{Li}^+$  diffusion pathways [25–30,36,37,41–44]. What's more, the unique three-dimensional hybrid nanostructure can form an effective three-dimensional electronically conductive network due to the excellent conductivity of RGO and MWCNTs-W. As a result, the RGO@MWCNTs-W/S with a three-dimensional hybrid

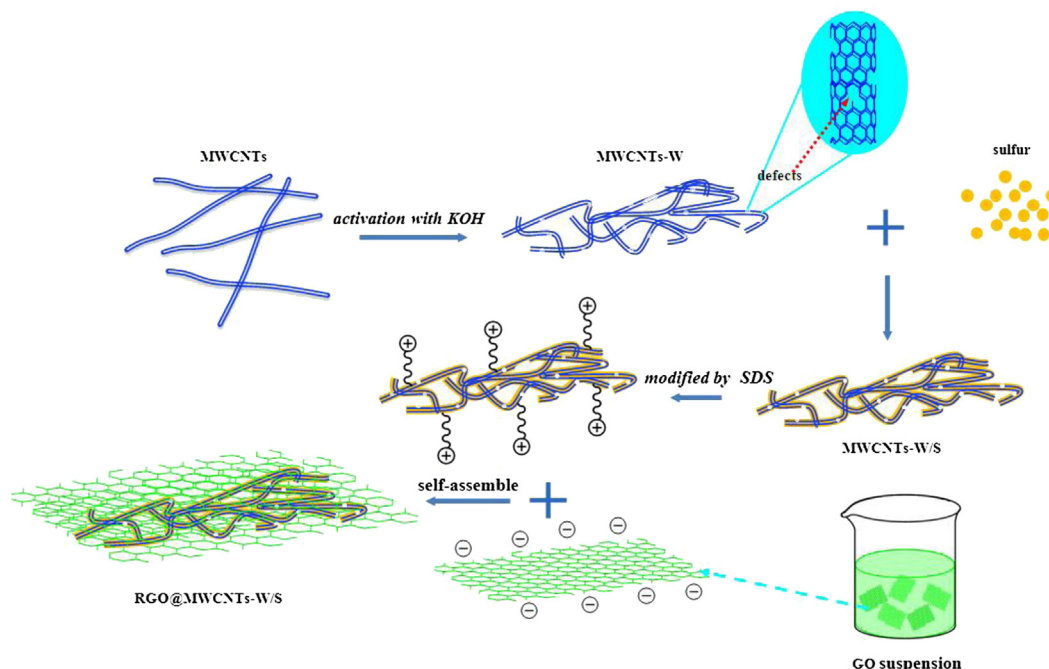


Fig. 1. The schematic diagram of the steps for synthesizing the RGO@MWCNTs-W/S composite.

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