



# Hydrothermal synthesis of boron-doped unzipped carbon nanotubes/sulfur composite for high-performance lithium-sulfur batteries



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## ABSTRACT

A boron-doped unzipped carbon nanotubes/sulfur (BUCNTs/S-1) composite was first prepared via a one-pot facile hydrothermal process by using oxidized unzipped carbon nanotubes (O-UCNTs), boron acid and element sulfur as the carbon precursor, B and S sources, respectively. The morphology, structure and composition of the BUCNTs/S-1 composite were characterized and the effect of B doping and sulfur loading were also investigated in details. The results demonstrated that the participation of B atom and sulfur loading achieved by hydrothermal method endowed the BUCNTs host with enhanced conductivity, promoted sulfur dispersibility and strengthened adsorbability for the sulfur species. The electrochemical performances of the BUCNTs/S-1 used as lithium-sulfur cathodes were then studied. Benefitting from all the merits, the BUCNTs/S-1 cathode delivered a high initial capacity of  $\sim 1251$  mAh/g at 0.2C, retaining as high as  $\sim 750$  mAh/g after 400 cycles, displaying significantly enhanced cycling stability. Hence, this work provides a facile method to fabricate a promising sulfur cathode candidate for high performance lithium-sulfur batteries.

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## 1. Introduction

With the rapid growth of the population and national economy, the development of renewable energy conversion and storage systems is desperately needed to solve the energy shortage crisis caused by the abuse of the limited fossil fuels [1]. Recently, lithium-sulfur batteries, as one promising candidate, have drawn much interest due to the high theoretical energy density of  $2600$  Wh  $\text{kg}^{-1}$  and the utility of low-cost, environmentally friendly and abundant sulfur as cathodes [2,3]. Despite these advantages, this kind of thriving battery system is still confronted with several issues. On one hand, the intrinsic insulating nature of the sulfur and the discharge product make slow electron transfer process, leading to very low utilization of active materials. On the other hand, the dissolution of the polysulfide intermediates in the organic electrolyte during the charge/discharge process, known as the “shuttle effect”, leads to rapid capacity decay and heavy loss of active materials [4,5].

Recently, many efforts have been dedicated to addressing these problems. One effective approach is to select a suitable conductive matrix to load and disperse sulfur particles [6]. The conductive matrix can not only improve the utilization of sulfur by making it electrically contacted, but also alleviate the severe dissolution of the polysulfide intermediates by suppressing them in the large internal surface of the conductive matrix. Carbon nanotubes (CNTs), as a typical one-dimensional carbon nanomaterial, have been widely investigated in the field of Li-S batteries for their intriguing electrical and mechanical properties [7–10]. The obtained CNTs/S cathode exhibited markedly improved electrochemical performance, which was attributed to the excellent conductivity and special physical confinement by the walls of nanotubes [11,12]. To further increase the surface area of CNTs for better adsorption of polysulfides, unzipped CNTs were also explored as sulfur host to enhance cycling performance of Li-S batteries [13]. However, the inherent nature defects of pristine CNTs hinder the electrochemical performance of the CNTs/S cathode still far from our demands. On one hand, the limited specific surface area and pore volume of pristine CNTs lead to serious agglomeration of sulfur particles. On the other hand, the inert surface of pristine CNTs enables weak adsorption of sulfur species, resulting in unsatisfied cycling performance.

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To effectively improve electrochemical performance of CNTs/S cathode, metal oxides or metal sulfides decorated carbon have been exploited as cathode materials. The inherently polar metal oxides/sulfides have been shown to strongly adsorb polysulfides [14,15]. However, the intrinsically low conductivity and high specific gravity of metal oxides/sulfides hinder further application to some extent. In addition, doping heteroatoms into carbon framework also proves to be very effective to adsorb sulfur species by altering the electronic structure and charge distribution to enhance cycling performance of Li-S batteries [16]. Among numerous heteroatoms, N doping has been widely investigated by far [17,18]. Huang et al. introduced a 3D nitrogen-doped graphene to serve as excellent conductive matrix and sulfur stabilizer by donating a lone pair of electrons, which can not only facilitate ion transport and electron transfer, but also create polarized active sites for adsorbing polysulfides, resulting in outstanding cyclic stability and greatly improved rate performance [19]. Apart from N atom, B, as electron-deficient counterpart to C, is another prospective dopant. Recently, Han et al. prepared B-doped graphene aerogel and demonstrated that the doped B atoms existed in carbon framework were electro-positive, leading to enhanced conductivity and strengthened chemisorption for the negatively charged polysulfides [20]. Therefore, heteroatom doping offers a valid way to improve the electrochemical performance of the sulfur cathode by altering the surface property of carbon matrix.

Another critical factor determining the electrochemical performance of C/S cathodes is the sulfur dispersion state on the carbon matrix. Generally, the more uniformly the sulfur loads, the higher the utilization rate of the active material, leading to better electrochemical performance. Generally, there are two main methods for sulfur loading, aqueous chemical reduction [21] and solid-state melt-diffusion [22]. The aqueous chemical reduction can achieve homogeneous distribution of sulfur particles on the surface of carbon matrix, but the preparation process is often complex and sulfur content in the resultant C/S composite can not be controlled exactly. While for the solid-state melt-diffusion method, the sulfur content in the C/S composite can be adjusted exactly, and the synthesis process is relatively simple and convenient. Nonetheless, it often suffers from heterogeneous dispersion of sulfur particles and poor sulfur electrical contacting upon the carbon surface, which can result in dissatisfactory utilization of active material. Recently, Cheng et al. for the first time reported a one-pot facile hydrothermal process to synthesize reduced graphene oxide/sulfur (rGO/S) composite as the cathode material, and the resultant reduced graphene oxide/sulfur cathode with cross-linking structure showed high specific capacity [23]. This method is simple and scalable, and the initial discharge capacity of the cathode is satisfactory, but the cyclability of this cathode still could not meet our demands for long-term cycling. Meanwhile, the influence of the hydrothermal process on the sulfur loading was not investigated in depth. Now that heteroatom doping can effectively promote cyclability of Li-S batteries, therefore it is of great interest to realize heteroatom doping during the sulfur loading process, which makes the process more convenient and enables better performance. To the best of our knowledge, so far there is no study to realize heteroatom doping during the sulfur loading by one-pot hydrothermal process.

Our previous research reported that oxidized unzipped carbon nanotubes (O-UCNTs) prepared by longitudinally splitting pristine CNTs were a good candidate for carbon precursor, because they possessed increased surface area and contained lots of oxygen-containing functional groups on their surface that could act as the active sites for subsequent heteroatom doping [24]. In this work, we fabricated B-doped unzipped carbon nanotubes/sulfur (BUCNTs/S-1) composite through a one-pot facile hydrothermal

process using the O-UCNTs, boron acid and element sulfur as the carbon precursor, B and S sources, respectively. The resultant BUCNTs/S-1 has the following merits. On one hand, sulfur was mixed with the BUCNTs by the one-pot facile hydrothermal process, enabling good sulfur dispersibility, excellent sulfur electrical contacting and high utilization of active material. On the other hand, successful B doping not only improves the conductivity of the carbon matrix, but also endows the BUCNTs with superior absorbability for sulfur species, which effectively retards the shuttle effect. As a result, the BUCNTs/S-1 cathode demonstrates outstanding cycling stability and rate capability.

## 2. Experimental

### 2.1. Synthesis of BUCNTs/S-1 and UCNTs/S composites

Firstly, the O-UCNTs were prepared by the modified Hummers' method reported previously [25]. 90 mg of O-UCNTs and 450 mg of boric acid were dispersed in water/ethanol mixture solution ( $v/v = 3/1$ ), and then the sulfur in  $CS_2$  solution was added into the mixture solution. After stirring continuously for an hour, the obtained mixture solution was transferred into a sealed 100 mL Teflon-lined stainless steel autoclave and maintained at  $180^\circ C$  for 12 h. After the hydrothermal reaction, the resultant viscous black suspension was filtered and washed with distilled water for several times, and the final product (BUCNTs/S-1 composite) was dried under vacuum at  $60^\circ C$  overnight. In contrast, the unzipped carbon nanotubes/sulfur (UCNTs/S) composite was prepared by the identical method without adding boron acid.

### 2.2. Synthesis of BUCNTs/S-2 composite

The B-doped unzipped carbon nanotubes/sulfur (BUCNTs/S-2) composite was also synthesized by two steps for comparison. Firstly, the BUCNTs were prepared by the above hydrothermal process without adding any sulfur source. Then the BUCNTs were mixed with element sulfur in an appropriate proportion and underwent the typical melt-diffusion process at  $155^\circ C$  for 12 h to get the BUCNTs/S-2 composite.

### 2.3. Material characterizations

Morphologies and structures of the samples were characterized by scanning electron microscope (SEM, Hitachi S-4800, Japan) and transmission electron microscope (TEM, JEM-2100F, Japan). X-ray diffraction (XRD) were measured using a X-ray diffractometer (Philips PC-APD) with Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) operating at 40 kV and 60 mA. Raman spectra were obtained in a Raman spectrometer (Labram-010, France) from  $50 \text{ cm}^{-1}$  to  $2000 \text{ cm}^{-1}$ . X-ray photoelectron spectroscopy (XPS) analysis was conducted with the ESCALAB250 XPS spectrometer with a Mg  $K\alpha$  X-ray source (1350 eV). The electrical conductivities of the electrodes were measured by a standard four point probe resistivity measurement system (RTS-9, Guangzhou, China). Thermogravimetric analysis (TGA) was performed in a simultaneous DSC-TGA analyzer (NETZSCH-409PC), and the samples were heated from room temperature to  $500^\circ C$  with a heating rate of  $5^\circ C/\text{min}$  under a continuous flow of  $N_2$  gas.

### 2.4. Electrochemical testing

Electrochemical testing was conducted using 2025 type coin cells with pure Li disk and polypropylene membrane as counter electrode and separator, respectively. 80 wt% C/S composite cathode material, 10 wt% Super P and 10 wt% polyvinylidene difluoride (PVDF) were mixed and stirred in N-methyl pyrrolidone

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