



Bi_2S_3 *in-situ* formed in molten S environment stabilized sulfur cathodes for high-performance lithium-sulfur batteries



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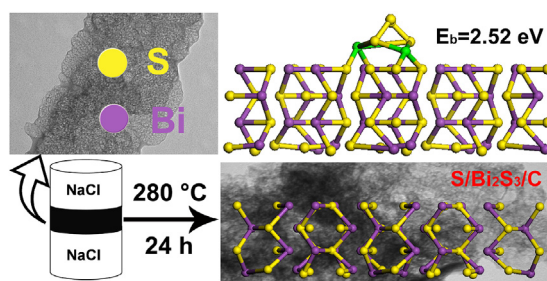
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HIGHLIGHTS

- A synchronous approach for S/ Bi_2S_3 /C composite cathodes is described.
- The *in-situ* formed Bi_2S_3 could provide anchoring effect with lithium polysulfides.
- Those S/ Bi_2S_3 /C composites exhibit good performance in Li–S batteries.

GRAPHICAL ABSTRACT



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ABSTRACT

S/ Bi_2S_3 /C composites have been prepared based on melt strategy at 280 °C starting from metallic bismuth (mp 271.3 °C), excess sulfur powder and porous carbon with different ratio. In the as-prepared composites, the *in-situ* formed Bi_2S_3 in molten S environment can homogeneously dispersed in S and carbon. Combining the physical confinement of porous carbon and chemical interaction of the *in-situ* formed Bi_2S_3 , the dissolution of polysulfides has been well inhibited. Thus, the obtained S/ Bi_2S_3 /C composite exhibits good electrochemical performance, which could deliver capacity of ~825 mAh g⁻¹ at 0.5 C over 400 cycles, with 91% capacity retention and high Coulombic efficiency.

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1. Introduction

To meet the growing demand of modern society for energy-storage devices, the lithium-sulfur (Li–S) battery system is currently under intensive investigation due to its high theoretical energy density (up to 2600 Wh kg⁻¹) [1,2]. Apart from the insulating nature of sulfur/polysulfides intermediates and volume change during cycling, the dissolution of polysulfides in electrolyte

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leads to loss of active materials and the shuttle reaction, which is the main problem to tackle with to make Li–S batteries feasible [3,4].

Traditionally, physical confinement using carbon materials varying from CMK-3 [5], micro- or meso-porous carbon [6,7], carbon nanotubes [8,9] to graphene [10,11] is the most common strategy employed in the design of host materials for the sulfur cathode. For example, Jayaprakash et al. prepared C@S nanocomposites based on mesoporous hollow carbon capsules, delivering a reversible capacity of 974 mAh g⁻¹ after 100 cycles at 0.5 C, with average Coulombic efficiency about 94%. The relatively low Coulombic efficiency should be caused by the dissolution of polysulfides during cycling [12]. In principle, such kind of physical confinement with poor adsorption capability could only slow down the diffusion rate, the polysulfides formed during cycling still can leach out into the electrolytes.

Recently, it has been proved by many works that the existence of chemical interaction between S/polysulfides species and host materials is important to achieve better cycling stability and Coulombic efficiency. To date, various types of such kind host materials have been discovered, including different metal oxides (TiO₂ [13], SiO₂ [14], Al₂O₃ [15], conductive Magnéli-Phase Ti_nO_{2n-1} nanomaterials [16], NiFe₂O₄ [17]), surface-modified carbon materials (nitrogen-doped mesoporous carbon [18], reduced graphene oxides [19]), metal organic framework [20] and so on.

For metal sulfides, Garsuch et al. firstly introduced TiS₂ in sulfur-carbon cathodes in Li–S batteries, and the TiS₂/sulfur/carbon composites could deliver ~700 mAh g⁻¹ after 100 cycles at 0.1 C [21]. While, the specific role of TiS₂ in TiS₂/S/C cathode during cycling was unclear and not studied. More recently, Li₂S/TiS₂ composites have been prepared by Cui and coauthors as cathodes for Li–S batteries [22], which showed electrochemical performance over 400 cycles, with Coulombic efficiency reach 98%. The authors declared that the improvement should be related to interaction between Li₂S and TiS₂. Metallic Co₉S₈ [23] and half-metallic CoS₂ [24] have also been adopted as host materials for Li–S batteries, which served as adsorption and activation sites for polar polysulfide intermediates, thus could accelerate redox reactions during cycling. Basically, for most of the approaches, the host materials are usually post-added to synthesis the final sulfur-based cathode composites. The *ex-situ* impregnation of sulfur into those hosts is limited to some extent, influenced by the host structure and surface chemistry, especially for such kind of chemical interaction or surface activated involved hosts.

In this study, we report the preparation of hybrid S/Bi₂S₃/C cathodes through simple melt strategy at 280 °C starting from commercial bismuth (mp 271.3 °C), excess sulfur powder and porous carbon, taking advantage of reaction activity between Bi and S in the molten system (2Bi+3S→Bi₂S₃, ΔG⁰ about -140.6 kJ mol⁻¹). Different from the previous host materials post-added strategies, the designed synthetic route provided the *in-situ* formation of Bi₂S₃ in excess melt sulfur atmosphere. Elementary sulfur content in the final composites was ranging from 61 wt% to 69 wt% by adjusting the ratio of the raw materials. The porous carbon in the composites ensures structural stability and fast electron transportation. The *in-situ* formed Bi₂S₃ afford binding effect with polysulfide intermediates, which has been proved by theoretical calculation and the comparison of their electrochemical property. As a result, when optimized the S content to 66 wt% in the final composite, best cell performance was achieved, with reversible capacities ~825 mAh g⁻¹ at 0.5 C over 400 cycles, and high rate capability of 528 mAh g⁻¹ at 5 C. Furthermore, the synthesis method to fabricate S/Bi₂S₃/C composite is relatively simple, which is suitable for the large scale production of high electrochemical performance S based cathodes materials.

2. Experimental section

2.1. Materials

All the chemical reagents used here were analytical grade without further purification.

2.2. Synthesis of C₄H₄MnO₆ derived porous carbon

The transition metal complex C₄H₄MnO₆ precursor [25] was annealed at 700 °C for 5 h under Ar atmosphere with heating rate of 5 °C min⁻¹. Subsequently, diluted HNO₃ was used to remove the unwanted MnO overnight to obtain the final porous carbon. Finally, the sample was further washed by distilled water and alcohol for at least five times and dried at 80 °C for 6 h.

2.3. In-situ synthesis of hybrid S/Bi₂S₃/C composites

To *in-situ* synthesis S/Bi₂S₃/C composites, commercial bismuth and sulfur powder with different molar ratio (S to Bi ranging from 24 to 48) were firstly mixed with the as-prepared porous carbon (carbon content about 20 wt%). Then the mixture was ball milled for 6 h with the assistance of water to form homogeneous slurry. After dried over night, the final products were obtained in a baked in salt approach we reported before [26], except the temperature was set as 280 °C considering the melting point of bismuth (271.3 °C).

2.4. Synthesis of S/C composites

For the S/C composites without Bi₂S₃, the preparation procedure is similar, except the adding of commercial bismuth.

2.5. Ex-situ synthesis of S/Bi₂S₃/C composites

To *ex-situ* synthesis S/Bi₂S₃/C composites, commercial bismuth and sulfur powder with different molar ratio of 2:3 were firstly mixed with the as-prepared porous carbon, and then sealed and heated at 280 °C for 24 h to obtain Bi₂S₃/C composite. Then, the as-prepared Bi₂S₃/C composite was mixed with sulfur powder and also heated at 280 °C (the selected temperature was to avoid other influence) for 24 h to obtain the final Bi₂S₃/C composite.

2.6. Material characterization

The crystal structures of the products were characterized using X-ray diffraction (XRD) measurements on a Philips X' Pert Super diffract meter with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). The scanning electron microscopy (SEM) studies were carried out on a JEOL-JSM-6700F emission SEM instrument, while transmission electron microscopy (TEM) images were measured on a field emission JEM-ARM 200F TEM instrument. Scanning electron microscope elemental mappings were obtained using a MERLIN Compact. Raman spectra were collected a LabRamHR Raman Microscope (laser wavelength = 514.5 nm) with samples pressed on the surface of a glass pane. X-ray photoelectron spectrometer (XPS) has been performed on ESCALAB 250 spectrometer (Perkin-Elmer) to characterize the surface state of electrodes. The XPS spectra were fitted with Gaussian-Lorentzian functions and a Shirley-type background. Sulfur 2p 3/2 and 2p 1/2 doublets are separated by 1.2 eV and their relative intensity is 2:1. Meanwhile, bismuth 4f 7/2 and 5/2 are separated from 5.3 eV and have an intensity ratio of 4:3. The binding energy values were all calibrated using the C 1s peak at 284.8 eV. The thermogravimetric analysis (TGA) was performed on a TA Instruments SDT Q600, with heating rate of 10 °C/min from

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