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Biomass derived $Ni(OH)_2$@porous carbon/sulfur composites synthesized by a novel sulfur impregnation strategy based on supercritical CO_2 technology for advanced Li-S batteries

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HIGHLIGHTS

- Porous carbon microspheres derived from yeast are fabricated by biotemplating method.
- Supercritical CO_2 technology is developed to impregnate sulfur into carbon matrices.
- Polar $Ni(OH)_2$ coating layer is designed to trap soluble polysulfides.
- $Ni(OH)_2$@PYC/S composite exhibits superior electrochemical performance.

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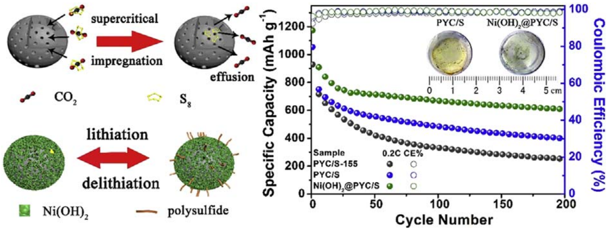
GRAPHICAL ABSTRACT



ABSTRACT

The rational design and controllable synthesis of sulfur cathode with high sulfur content, superior structural stability and fascinating electrochemical properties is a vital step to realize the large-scale application of rechargeable lithium-sulfur (Li-S) batteries. However, the electric insulation of elemental sulfur and the high solubility of lithium polysulfides are two intractable obstacles to hinder the success of Li-S batteries. In order to overcome aforementioned issues, a novel strategy combined supercritical CO_2 fluid technology and biotemplating method is developed to fabricate $Ni(OH)_2$ modified porous carbon microspheres as sulfur hosts to ameliorate the electronic conductive of sulfur and enhance simultaneously the physical and chemical absorptions of polysulfides. This elaborately designed $Ni(OH)_2$@PYC/S composite cathode exhibits high reversible discharge capacity (1335 mAh g^{-1} at 0.1 C), remarkable cyclic stability (602 mAh g^{-1} after 200 cycles at 0.2 C) and superior rate capability, which is much better than its PYC/S counterpart. These results clearly demonstrate that the advanced porous carbon with good conductivity and the polar $Ni(OH)_2$ coating layer with strong trapping ability of polysulfides are responsible for the enhanced electrochemical performance.

1. Introduction

Rechargeable Li-ion batteries (LIBs) have many merits, such as low cost, high capacity and long life, which are the most promising energy storage devices that have been widely used in portable electronic devices and hybrid electric vehicles [1,2]. However, the traditional Li-ion batteries mainly composed of transition metal oxide cathode (e.g. $LiCoO_2$) and graphite anode are approaching the limitation of their

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theoretical energy densities. Therefore, it is crucial to explore the next generation of high energy density storage system. In this regard, Li-S batteries receive considerable attention owing to the unparalleled advantages of sulfur cathodes, such as high theoretical specific capacity (1675 mAh g^{-1}), low cost (110 USD per ton), and excellent environmental friendliness [3,4]. Despite of the desirable advantages, the main bottleneck of the large-scale commercial application of Li-S secondary battery can be concluded as follows. Firstly, both sulfur and lithium sulfides are insulators, resulting in low reaction kinetics and poor rate performance. Secondly, the volumetric expansion during the lithiation process due to the large difference in the densities of S (2.03 g cm^{-3}) and Li_2S (1.67 g cm^{-3}) will greatly deteriorate the structural stability and cyclic stability of sulfur electrode [5]. Thirdly, the dissolution and shuttle of reactive intermediates of lithium polysulfides (Li_2S_x, $4 \le x \le 8$) will reduce the utilization of active substances, leading the low Coulombic efficiency [6,7]. Up to now, tremendous strategies have been developed to make sulfur cathode more applicable in Li-S batteries, which can be generally grouped into three categories. (i) Adding conductive agent to improve the conductivity of sulfur and its reduced products. (ii) Applying various porous structures and buffer additives to ease the volume effect. (iii) Creating physical/chemical adsorption to trap the dissolution of soluble polysulfide intermediates [8–10].

Among the aforementioned approaches, carbon materials with high specific surface area, abundant porous structure, large pore volume and excellent electric conductivity have been considered as key materials to achieve high performance sulfur cathode [11–13], such as activated carbon [14,15], carbon nanotube [16], mesoporous carbon [17], and graphene [18,19]. In this respect, Zhang et al. demonstrated the rational hybridization of sp^2 graphene/CNT and nanostructured porous carbon as advanced sulfur hosts for Li-S batteries [20]. It offers an effective method to combine the sp^2 nanocarbon with nanostructured carbon for synthesizing advanced sulfur cathode with high energy density and long cycling life. However, the synthesis of state-of-the-art carbon materials for sulfur cathodes typically requires exotic hard templates and/or expensive surfactants with complex procedures. Considering the environmental factor and economic benefit, biologic materials as sustainable carbonaceous sources have drawn widespread attention due to their incomparable advantages of easy availability, low cost, excellent renewability and environmental friendliness [21]. Particularly, our group has successfully exploited various biomass to synthesize carbon-based electrode materials, including microalgaes [22–25], bamboo [26–29], pollen [30,31] and kapok fibers [32–37]. Therefore, it is highly expected that biomass derived carbon materials will be the promising sulfur hosts in Li-S batteries.

Apart from the selection of host materials for sulfur, the method for storing sulfur is also a key factor in Li-S battery. Although various methods have been adopted to synthesize sulfur/carbon composites, the routine methods (e.g., melt-diffusion method) not only are difficult to achieve the uniform distribution of sulfur and full utilization of porous carbon matrices, but also involve highly toxic solvent (e.g., carbon disulfide (CS_2)) and high energy consumption of manufacturing processes. Hence, the exploration of green and efficient methods to prepare advanced sulfur/carbon composites is extremely urgent. Owing to the "gas-like" and "liquid-like" physicochemical properties, supercritical CO_2 fluid has high infiltrability, fast diffusivity and powerful solvability, which can be considered as a cheap, clean and nontoxic solvent to synthesize various functional composite materials [24]. Thereby, it can be imagined that the successful implementation of supercritical CO_2 method to fabricate sulfur/carbon composites may have incomparable merits to routine method. Firstly, different from the traditional strategies (e.g., melt-diffusion method), supercritical CO_2 method only uses cheap, clean and nontoxic CO_2 as solvent and reaction media, which could replace the highly toxic and expensive CS_2 solvent commonly used in melt-diffusion method. Secondly, the reaction temperature of supercritical CO_2 is 32 °C that is much lower than melt-diffusion method (155 °C). More importantly, owing to the high penetration, high diffusivity and high dissolving capacity of supercritical CO_2 fluid, sulfur can easily reach to inner pores of carbon matrices and form the uniform distribution. Thus, it makes a full utilization of carbon matrices with high specific surface area and abundant porous structure.

Constructing sulfur/carbon composite cathodes could significantly improve the electrical conductivity and structural stability of sulfur cathode, however, it still could not overcome the never-ending dissolution and shuttle of reactive polysulfide intermediates because of the weak physical adsorbing ability of nonpolar carbon matrices for trapping highly polar polysulfides. Therefore, rationally establishing the strong chemical bonds between polysulfides and hosts is essential to alleviate the shuttle of polysulfides. Recently, polar additives such as MnO_2 [38–40], Ti_4O_7 [41,42], SiO_2 [43,44], hydroxides [45–48], heteroatom dopants [49,50] and polymers [51] present fascinating potential for strongly trapping polysulfides. For instance, Rubha Ponraj et al. reported the surface modification of active sulfur by MgO nanoparticles [52]. The strong interactions between MgO nanoparticles and polysulfides can enhance the utilization of sulfur and increase the cycling stability of lithium-sulfur batteries. Therefore, the combination of sulfur/carbon materials with high conductivity and polar surface modifiers with strong chemical adsorption may be a promising strategy to address the intractable issues of sulfur cathode in Li-S batteries.

In this work, we are devoted to developing a new kind of hydroxide surface modified carbon/sulfur composites *via* a biotemplating method with the assistance of supercritical CO_2 fluid technology for superior sulfur cathodes in Li-S batteries as shown in Fig. 1. Natural yeasts [53,54] are employed as both biological templates and renewable carbon sources to fabricate high conductivity porous carbon matrices for encapsulating sulfur. After the supercritical CO_2 treatment, sulfur can be successfully impregnated into porous carbon matrices to construct sulfur/carbon composites. Meanwhile, nickel hydroxide ($Ni(OH)_2$) nanoparticles serve as surface modifiers to enhance the chemisorption for polysulfides and suppress the migration of sulfur. Thereby $Ni(OH)_2$ outer layer is tightly adhered on the surface of porous yeast carbon/sulfur (PYC/S) composite to form a novel core-shell structure. Owing to this rationally unique structure, $Ni(OH)_2$@PYC/S presents remarkably enhanced electrochemical performance to other counterparts.

2. Experimental

2.1. Material synthesis

Pretreatment of yeast cells: 5 g yeast powder was firstly immersed into deionized water for 30 min. The awakened yeast cells were added into 50 ml mixed solution composed of alcohol and formaldehyde (1:1 in volume), and then violently stirred for 30 min to fix cell morphology. After that, the fixed yeast cells were centrifuged and washed by deionized water and dried in an oven at 80 °C overnight.

Synthesis of porous yeast carbon: Porous yeast carbon (PYC) were prepared as follows. 2 g $NiSO_4 \cdot 6H_2O$, 1 g hexamethylenetetramine and

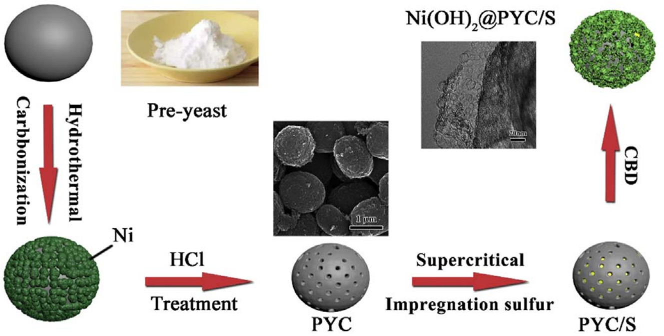

Fig. 1. Schematic illustration of the synthesis process of $Ni(OH)_2$@PYC/S composites.