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Facile synthesis of hierarchically γ-Al_2O_3@C yolk-shell microspheres for lithium-sulfur batteries

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HIGHLIGHTS

- γ-Al_2O_3@C yolk-shell microspheres were synthesized.
- γ-Al_2O_3@C yolk-shell structure can encapsulate the polysulfides.
- There is a synergistic action among C and γ-Al_2O_3.
- Sulfur cathodes containing γ-Al_2O_3@C yolk-shell microspheres exhibit high initial discharge capacity.
- Sulfur cathodes containing γ-Al_2O_3@C yolk-shell microspheres exhibit a superior rate performance.

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ABSTRACT

The practical application of lithium-sulfur batteries (LSBs) remains restricted because of a severe polysulfide-shuttle effect and the insulating nature of sulfur. In this work, a kind of unique γ-Al_2O_3@C yolk-shell microspheres comprising carbon coating on the γ-Al_2O_3 yolk-shell microspheres were synthesized using organic adsorpting and in-situ thermal reduction methods, and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM). It was demonstrated that the γ-Al_2O_3@C yolk-shell microspheres could encapsulate the polysulfides and increase the sulfur utilization. Accordingly, γ-Al_2O_3@C yolk-shell microspheres cathode achieved high initial discharge capacity of 1046.9 mAh g^{-1}, excellent discharge capacity (765.5 mAh g^{-1}) after 70 cycles (the capacity retention was about 73%) and superior rate performance. In addition, the appropriate C content was proved to be an important factor in the influence of electrochemical performances. Hence, our present method paves a new path to improve the performance of Li—S batteries.

1. Introduction

Recently, with the development of energy storage devices, rechargeable batteries with high performance have been attracted more and more attention. Among all rechargeable batteries, the lithium-sulfur battery has been widely believed to be one of the most promising devices for next-generation energy storage systems due to its high theoretical energy density (2600 Wh kg^{-1}), specific capacity (1675 mAh g^{-1}) and the low price of raw materials [1,2]. However, there are still many problems that plague practical application of lithium-sulfur batteries, including the "shuttle effect" resulting from the dissolution of lithium polysulfide produced during the discharge/charge process and the low utilization of sulfur attributing to high resistivity of elemental sulfur and its other products.

In order to deal with these problems, a variety of efforts have been made toward improving the electrochemical performances of Li—S batteries in recent years. The most popular strategy has been developing various types of carbonous materials to suppress the "shuttle effect" and promote inferior conductivity, including porous carbon [3–6], single-walled or multi-walled carbon nanotubes [7,8], active carbon [9,10], conductive polymers [11–14], graphene-based nanomaterials [15] However, It should be indicated that the nonpolar conductive carbon materials has no sufficiency to diminish the polysulfide-shuttle effect due to the high-polar nature of polysulfides. The second strategy has been developing polar materials (metal sulfides [16–18] and metal oxides [19,20] et al.) to improve the electrochemical performances by strong absorbing lithium polysulfides during charge-discharge process, but there is a low utilization of sulfur because of their relatively high resistivity. The third effective strategy is to development hybrid composites of carbon and polar materials. For example, Yolk-

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Shelled C@Fe_3O_4 and Co-VN@C showed excellent performances owing to the physical confinement of the diffused polysulfides [21,22].

Al_2O_3 is found to trap polysulfides via producing a strong chemical raction by Choi [23]. This electrodes containing nano-sized Al_2O_3 exhibits higher discharge capacity than that of the sulfur electrode without nano Al_2O_3. Dong et al. [24] reported micron-sized flaky Al_2O_3 as the adsorbent to reduce the dissolution of polysulfides into electrolytes. Besides these diverse structures, the designation and application of enclosed yolk-shell-structured γ-Al_2O_3@C as host materials have not been reported to date. The yolk-shell structures displayed much improved cycle ability due to their benefits of low density, favourable specific surface area and enclosed structure characteristics.

Here, γ-Al_2O_3@C yolk-shell microspheres have been obtained using Congo red (CR) adsorption and in-situ thermal reduction methods. Benefiting from the unique yolk-shelled structure, γ-Al_2O_3@C yolk-shell microspheres has the following advantageous features: (i) This yolk-shell structure can encapsulate the polysulfides. (ii) The large void space of γ-Al_2O_3@C not only restricts large volume expansion during the cycling but also improves the sulfur utilization. (iii) There is a synergistic action among C and γ-Al_2O_3. Moreover, the obtained γ-Al_2O_3@C yolk-shell microspheres electrode showed excellent electrochemical performances and achieved long-cycling stability.

2. Experimental section

2.1. Preparation of γ-Al_2O_3 yolk-shell microspheres

In a typical preparation, γ-Al_2O_3 yolk-shell microspheres were synthesized by a simple hydrothermal method. 40 mmol of glucose ($C_6H_{12}O_6$), 30 mmol of urea ($CO(NH_2)_2$) and 7.5 mmol of aluminum ammonium sulfate ($NH_4Al(SO_4)_2{\cdot}12H_2O$) were added to 140 mL of deionized water under tirring, the mixed solution was then transferred to a Teflon-lined stainless steel autoclave, followed by heated to 180 °C for 6 h in an oven. After cooling to room temperature, a brown product was separated by filtration and washed with deionized water and anhydrous alcohol several times, then it was dried in a vacuum oven at 60 °C for 12 h. Finally, the γ-Al_2O_3 yolk-shell microspheres were obtained by the calcination for precursor at 600 °C for 3 h in air.

2.2. Preparation of γ-Al_2O_3@C yolk-shell microspheres

The as-synthesized γ-Al_2O_3 yolk-shell microspheres (0.5 g) were mixed with different concentration of CR solution (100 ml; 100 mg/L, 300 mg/L, 500 mg/L) with magnetic stirring for 2 h. Subsequently, the γ-Al_2O_3@CR yolk-shell microspheres were harvested through centrifugation and vacuum dried at 60 °C for 12 h. Finally, the γ-Al_2O_3@C yolk-shell microspheres (marked as γ-Al_2O_3@C-100, γ-Al_2O_3@C-300 and γ-Al_2O_3@C-500, respectively) were annealed at 600 °Cfor 2 h in N_2 with a heating rate of 2 °C min^{-1}.

2.3. Preparation of the sulfur composite

Firstly, 0.3 g S, 0.08 g Super P and 0.02 g CoS_2 (the synthetic process was presented in Supporting Information) were mixed sufficiently before putting in a covered crucible. Then the covered crucible was transferred to a 200 mL Teflon-lined stainless-steel autoclave and maintained at 155 °C for 6 h. The sulfur composite was obtained after cooling to room temperature.

2.4. Materials characterization

The phase and morphology structure were characterized by Powder X-ray diffraction (DX-2700 diffractometer with a Cu-Kα radiation source), JSM-6490LV (JEOL, Japan) and Nova Nano SEM230 (FEI, America) scanning electron microscope.

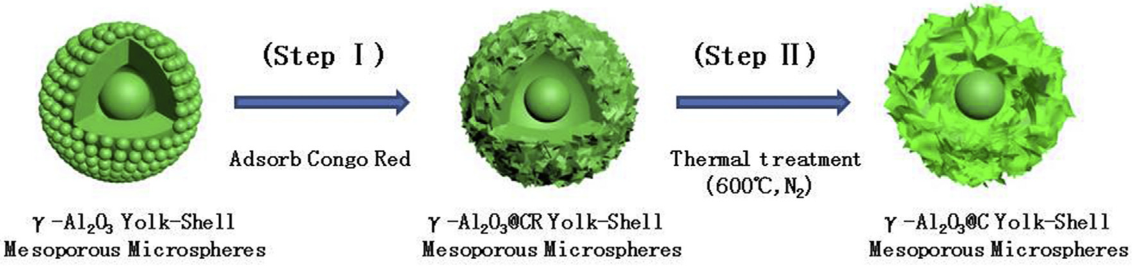
2.5. Electrochemical measurement

The Cyclic voltammetry (CV) and electrochemical impedance spectroscopy measurements were measured BTS4000 cell test instrument (Shenzhen Neware, China). Sulfur composite (70 wt %), γ-Al_2O_3@C (−100, −300 and −500, respectively) yolk-shell (10 wt %), Super P (10 wt %) and polyvinylidene fluoride (PVDF) binder (10 wt %) were mixed in N-methyl-2-pyrrolidinone to form a uniform slurry. This slurry was then casted onto aluminium foil using doctor blade and dried under a vacuum oven at 60 °C for 12 h to form the Li—S cathode. The electrolyte was made up of 1M LITFSI, 0.1M lithium nitrate ($LiNO_3$) in 1, 2-dimethoxyethane (DME) and 1, 3-dioxolane (DOL) (volume ratio 1:1). The batteries were assembled in an Ar-filled glove box. A loading mass of sulphur was 0.96 mg/cm^2. CV curves were detected in the voltage range 1.5–3 V. The electrochemical impedance was tested in the frequency range of 0.01 Hz–100 k Hz. As comparison, the sulfur cathodes containing γ-Al_2O_3 yolk-shell mesoporous microsphere (Sulfur composite: Al_2O_3: Super P: PVDF = 7:1:1:1) and sulfur cathode containing without Al_2O_3 (Sulfur composite: Super P: PVDF = 7:2:1) were prepared in the same method and tested under same condition.

3. Results and discussion

The formation mechanism of γ-Al_2O_3@C yolk-shell microspheres is illustrated in Scheme 1. In the Step I, hierarchically γ-Al_2O_3@CR yolk-shell microspheres were prepared by the adsorption of Congo red on the surface of γ-Al_2O_3 yolk-shell microspheres. In the step II, the γ-Al_2O_3@CR yolk-shell microspheres were calcined at 600 °C in N_2, resulting in the formation of γ-Al_2O_3@C yolk-shell mesoporous microspheres.

The crystal structures of as-prepared materials were investigated by X-ray diffraction (XRD). As shown in Fig. 1a, the XRD of three yolk-shell microspheres samples were identical, and all were indexed to the cubic γ-Al_2O_3 (JCPDS Card 10–0425). The morphology and microstructures were then measured by SEM. Fig. 1b showed a typical SEM image of γ-Al_2O_3 yolk-shell mesoporous microspheres, from which one can see that the obtained yolk-shell architecture with a diameter of 3–4 μm and a granular surface. Although the γ-Al_2O_3@CR yolk-shell microspheres (Fig. 1c) and γ-Al_2O_3@C yolk-shell microspheres (Fig. 1d) retained an intact yolk-shell structure and similar size, there was an appearance of



Scheme 1. Schematic illustration of the synthesis of hierarchically γ-Al_2O_3@C yolk-shell mesoporous microspheres.