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Regular Article

Cobalt fibers anchored with tin disulfide nanosheets as high-performance anode materials for lithium ion batteries

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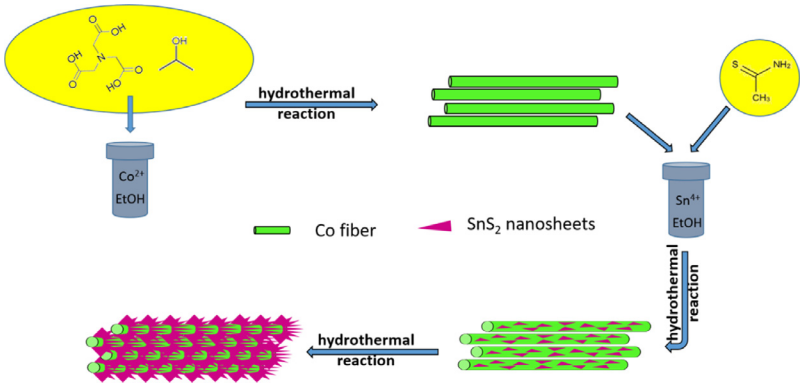
GRAPHICAL ABSTRACT



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ABSTRACT

Well-designed hierarchical nanostructured composites consisting of one dimensional cobalt fibers and thin tin disulfide nanosheets were successfully synthesized for the first time through a hydrothermal method. The SnS_2 nanosheets were uniformly grown onto the Co fibers and were almost perpendicular to the Co fibers. The composites as one kind anode materials exhibited more remarkable lithium ion storage properties than SnS_2 nanosheets. The composites exhibited a capacity of 500.5 mA h/g after 100 cycles even at 1000 mA/g. The improved electrochemical performance could be assigned to the Co fiber substrate support, which could provide short lithium ion and electron pathways, alleviate large volume expansion, contribute to the capacity, and offer mechanical stability for the anode electrode. This special designing perhaps could lay a foundation for the preparation of high performance lithium ion battery anode materials.

1. Introduction

In recent years, the large amount energy consumption because of the rapid urbanization and industrialization resulted in severely air pollution problems [1,2]. Development novel energy storing

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equipment possessing high specific capacities as well as good cycle performance has been drawn more and more interesting [3]. As one kind promising energy storage devices, lithium ion batteries have been widely studying because of high-energy densities, their safety, non-pollution and long-term life [4]. However, commercial graphite-based anode materials are difficult to meet the requirements in the application of high power area because of the relatively low theoretical specific capacity (372 mA h/g) as well as the lack of shape flexibility [5,6]. A lot of efforts have been focused on seeking new kind of anode materials with remarkable specific capacity, long-term life and excellent rate performance.

Recently, sn-based anode materials, such as SnS_2 has been widely studied because of its relatively high capacity and the layered CdI2-type structure, which is favorable to buffer the volume change in the process of alloying and dealloying [7–9]. As known that Li/Sn alloys ($Li_{4.4}Sn$) have a specific theoretical discharge capacity of 990 mA h/g, which is much higher than the capacity of the commercialized graphite-based anode materials. Additionally, the layered CdI2-type nanostructure could fasten the diffusion of lithium ions and electrons and buffer volume expansion to some degree owning to the existence of the swelling tolerant hosting spaces [10]. However, the capacity fading of sn-based electrode materials is still severe because of the large volume changes as well as the poor electrical conductivity [11].

Combination with some electronically conductive materials, including CNTs, graphene or noble metals was considered a valid approach to increase the conductivity of sn-based anode materials [12–14]. Likewise, morphology controlled preparation of nanostructured composites, such as nanobelts, nanosheets, nanorods, nanowires and nanotubes was considered another effective approach to improve cells' performance and stability [15–20]. Special nanostructure designing of anode materials could not only fasten the diffusion of Li^+ but could compensate the large volume changes in the process of Lithium ions insertion/extraction because of large surface-to-volume ratio [20]. For examples, Zhang synthesized the CNTs@SnO_2 hybrid nanocomposites through loading SnO_2 nanoparticles onto CNTs network with cross-stacked structure, which showed outstanding lithium storing properties [21]. Yue [22] facilely prepared Mn_3O_4-coated carbon nanofibers on copper foam, which exhibited high special capacity and long cycle ability. Zhao [23] used single-walled carbon nanohorns coated with Fe_2O_3 as a superior anode material, which exhibited good rate performance and good cycle stability at a high density of 1000 mA/g.

Here, we prepared a novel SnS_2 nanosheets decorated Co fiber hybrid structures by simple hydrothermal reactions, and the growth mechanism of the novel Co fibers @SnS_2nanosheets was presented in Fig. 1. In which, 2D SnS_2 nanosheets provided the active sites for the accommodation of Li^+ and buffer the volume change, and Co fibers served as a mechanical support could increase the electrical conductivity and prevent active anode materials agglomeration. Consequently, the Co fibers @SnS_2 nanosheets exhibited a higher discharge specific capacity and a better cycle stability compared with the pure SnS_2 nanosheets.

2. Experiment

2.1. Sample preparation

In order to prepare the cobalt fibers, 0.02 mol cobalt chloride ($CoCl_2{\cdot}6H_2O$) and 0.01 mol nitrilotriacetic acid ($N(CH_2COOH)_3$) were mixed with a solution containing 54 mL of distilled water and 18 mL of isopropanol. After stirred for 1 h, the solution was poured into a 100 mL closed container, then heated 6 h at 180 °C. When to the temperature decreased, the products were cleaned repeatedly with distilled water and absolute ethyl alcohol, respectively. After dried at 60 °Cfor 12 h in a vacuum, the cobalt nanofibers (Co fiber) can be obtained.

For the synthesis of Co fibers@SnS_2 nanosheets core–shell composites, 1 mmol Co nanofibers were completely dissolved in 75 mL of absolute ethyl alcohol by ultrasound. Then 0.7 g Tin (IV) chloride dehydrate ($SnCl_4{\cdot}5H_2O$) and 0.6 g thioacetamide (CH_3CSNH_2) were added and then stirred for 1 h. Then poured the solution into a closed container and was kept at 180 °C for 24 h. When cooled down to room temperature, the obtained samples were respectively cleaned by ultrapure water as well as absolute ethyl alcohol, then dried for a night at 60 °Cin a vacuum.

2.2. Materials testing

The crystalline nanstructure of Co fibers @SnS_2nanosheets was investigated through X-ray diffraction (XRD, model D/max-2500 system, Rigaku.). Morphology of Co fibers @SnS_2nanosheets composites was observed using a scanning electron microscope

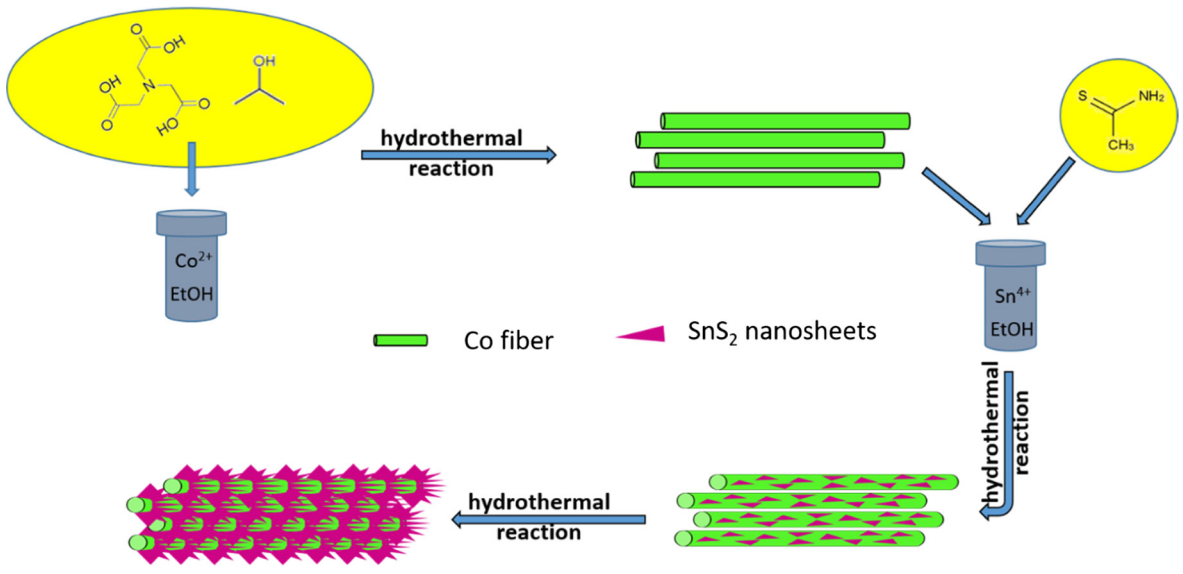

Fig. 1. Formation mechanism of the Co fibers @SnS_2 nanosheets core–shell composites.