



Sheet-on-sheet chrysanthemum-like C/FeS microspheres synthesized by one-step solvothermal method for high-performance sodium-ion batteries



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HIGHLIGHTS

- Chrysanthemum-like C/FeS microspheres are synthesized by one-step solvothermal method.
- FeS nanosheets and carbon nanosheets are with 2D sheet-on-sheet structure.
- 2D C/FeS nanosheets are self-assembled to form a 3D chrysanthemum-like morphology.
- The microspheres show excellent sodium-storage performance of 500 mAh g⁻¹ at 0.2 A g⁻¹.

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ABSTRACT

Chrysanthemum-like carbon/FeS microspheres (CL-C/FeS) are prepared from a one-step solvothermal method. The morphology and structure of the CL-C/FeS are characterized by X-ray diffraction, scanning electron microscopy and high-resolution transmission electron microscope. We note that the prepared CL-C/FeS microspheres exhibit the average diameter of 15 μm and possess a sheet-on-sheet structure. FeS nanosheets are stacked on the carbon sheets to form a 2D sheet-on-sheet structure, these 2D C/FeS nanosheets are self-assembled to form a 3D chrysanthemum-like morphology. Due to the unique structure, CL-C/FeS microspheres show the excellent sodium-storage performance of 500 mAh g⁻¹ at 0.2 A g⁻¹ and 260 mAh g⁻¹ at 1 A g⁻¹, which are higher than those of most reported values. Therefore, the CL-C/FeS with appropriate structure is expected to be a competitive choice for anode materials for sodium ion batteries.

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1. Introduction

Lithium-ion batteries (LIBs) have been successfully utilized in portable electronic devices and electric vehicles because of their high-energy density and power density [1,2]. In recent years, lithium resource is becoming increasingly expensive due to the limited resource and heavy demand [3,4]. Meanwhile, sodium resource, as the most abundant, geographically ubiquitous, and potentially cheap resource in the Earth's crust and ocean, gives sodium-ion batteries a promising future for the large-scale application in electrical energy storage [5–10]. Hence researches on sodium-ion batteries (SIBs) have gained momentum in recent years

[5,7–10]. Up to now, there are numerous materials that can be used as the anode materials of SIBs, for instance, carbonaceous materials, including mesoporous soft carbon [11], carbon spheres [12–14], heteroatom-doped carbons [15–18] and the carbon-containing composites [19–24]. What's more, transition metal compounds including oxides [25], sulfides [26,27], and fluorides [28] have attracted a lot of attention due to their high specific capacities, low cost, and facile producibility [29–31].

Among the various anode materials of SIBs, the metal sulfides have also been regarded as a most promising class of high capacity materials [5,21,32,33]. The newly emerging sodium-metal sulfide batteries, including FeS [22,34], FeS₂ [5,6], SnS₂ [35], Ni₃S₂ [36], Sb₂S₃ [37], have risen to prominence owing to their high rate performances and specific capacities. Iron sulfide has recently been considered as a promising anode material by many researchers because of its high theoretical capacity, cost effectiveness,

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environmental friendliness and abundance in nature [38,39]. However, iron sulfide suffers largely from the large volume change during the insertion and extraction of Na ions [6,7,9,40]. Kim et al. [6] prepared pyrite in an FeS₂/Na battery but the capacity decreased fast from 630 to 85 mAh g⁻¹ after 30 cycles. The morphology of FeS had been changed to an agglomerated shape during the charge/discharge processes, and the agglomerated shape could not recover to the original one by charge process, which means the irreversible transformation. In another hand, the low conductivity and sluggish kinetics of FeS always give rise to the inferior electrochemical properties [22]. Thus, in order to enhance the electrochemical performance of FeS, the above-mentioned problems should be considered. For example, Wang et al. [22] synthesized the uniform yolk-shell iron sulfide–carbon nanospheres as anode materials for SIBs [22]. The porous carbon shells help to improve the conductivity, and the hollow layer contributes to relieve volume expansion. Owing to the unique structure, the spheres can reach a capacity of 545 mAh g⁻¹ (0.1 A g⁻¹) with the first coulombic efficiency of 70.2% [22].

In this work, we proposed an effective strategy to improve the electrochemical performances of FeS by using FeS nanosheets covering on a carbon layer. A new kind of 3D chrysanthemum-like carbon/FeS microspheres were synthesized via an efficient one-step surfactant-assisted solvothermal-based approach. FeS nanosheets and carbon nanosheets were stacked closely to form a sheet-on-sheet structure, the 2D sheet-on-sheet FeS/C nanosheets were self-assembled to form a 3D interconnected structure with a chrysanthemum-like morphology. Owing to the unique structure, the 3D chrysanthemum-like carbon/FeS microspheres (abbreviated as CL-C/FeS below) show an initial reversible capacity of 661 mAh g⁻¹ at 0.2 A g⁻¹, and retain an excellent capacity of 500 mAh g⁻¹ after 45 cycles. Moreover, the composites maintain a capacity of 260 mAh g⁻¹ at a high current density of 1 A g⁻¹ after 200 cycles. Therefore, the CL-C/FeS with appropriate structure is expected to be a competitive candidate for anode materials of sodium-ion batteries. Meanwhile, the efficient one-step chemical method to prepare the carbon/iron sulfide composites makes our work more competitive with the others [22,34].

2. Experimental section

2.1. Material synthesis

In a typical synthesis, ferrocene, thiourea and surfactant PEG-200 were firstly dissolved into the ethylene glycol with a molar ratio of 1: 4: 0.1, then the mixtures were added into a Teflon-lined sealed autoclave and maintained at 180 °C for 24 h to get the precursor. Finally, the precursor was annealed at 600 °C for 3 h under the pure nitrogen gas atmosphere to obtain the chrysanthemum-like C/FeS microspheres. We also prepared the pure carbon materials (contrast sample CL-C) by handling the CL-C/FeS in aqueous hydrochloric acid solution with the concentration of 4 mol/L for comparison. In addition, a commercial FeS (bought from Sinopharm Chemical Reagent Beijing Co., Ltd) was used for comparison without post-treatment. All the above reagents were analytical grade without further purification.

2.2. Characterization

The crystal structures were characterized by X-ray diffraction (XRD, Rigaku D/max-2500B2+/PCX system) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) over the range of 5–90° (2 θ) and Raman spectroscopy (Renishaw inVia Reflex using 514 nm laser excitation) at room temperature. Moreover, thermogravimetric analysis (TG) was measured by a NETZSCH STA 449C analyzer with the heating rate of

10 °C min⁻¹ under an air atmosphere. The morphologies and structures of the samples were characterized by field emission scanning electron microscopy (FESEM, ZEISS SUPRATM 55) and high resolution transmission electron microscopy (HRTEM, Tecnai G2 F20 UTWIN electron microscope with an accelerating voltage of 300 kV). Brunauer–Emmett–Teller (BET) model was measured to get the specific surface areas (SSAs), and the density functional theory (DFT) method was used to get the pore size distribution.

2.3. Electrochemical measurements

The working electrodes were prepared by mixing active material, carbonaceous additive (acetylene black), and polyvinylidene difluoride (PVDF) at a weight ratio of 8: 1: 1, and a few drops of *N*-methyl-2-pyrrolidinone (NMP) were added to form a slurry. The slurry was coated onto nickel foams and then the electrodes were dried under 120 °C for 12 h in the vacuum oven and pressed at 10 MPa for 5 min. The electrodes were tested using the CR2025 type cells, which were assembled in an argon-filled glove box (M Braun, concentrations of moisture and oxygen are below 1 ppm). The counter electrodes were sodium plates, and the electrolyte was 1 M NaSO₃CF₃ solution in diglyme. The galvanostatic charge/discharge tests of the cells were measured under a voltage window between 0.01 V and 3.0 V at various current densities from 0.1 A g⁻¹ to 5 A g⁻¹ using the LAND-CT2001A battery testing system. Cyclic voltammetry (CV) measurement was tested at a scan rate of 0.1 mV s⁻¹ in the range of 0.01–3.0 V on a Zennium electrochemical workstation. Electrochemical impedance spectroscopy (EIS) was tested with the frequency range of 0.01–100 kHz with an amplitude of 5 mV.

3. Results and discussion

Fig. 1a illustrated the growth process of the 3D chrysanthemum-like C/FeS microspheres. FeS nanosheets are prepared in the presence of carbon resource. FeS nuclei is formed at the high autogenous pressure inside the sealed reaction vessel and meanwhile the carbon nanosheet is in situ grown around FeS nuclei due to the catalysis of FeS. With the continuous reaction, FeS nanosheets are naturally attached with the carbon nanosheets tightly. Therefore FeS/C composited nanosheets with unique 2D sheet-on-sheet structure are obtained. Then the FeS/C composited nanosheets are self-assembled in solution to form the 3D chrysanthemum-like C/FeS microspheres.

Fig. 1b shows the XRD patterns of the commercial FeS and CL-C/FeS. All the diffraction peaks of the CL-C/FeS are exclusively attributed to FeS (JCPDS 65–9124). By the calculation with the Scherrer's formula, the average grain diameter of FeS is 46.3 nm. No visible peaks of crystalline carbon are detected in CL-C/FeS, indicating the amorphous carbon structure. The Raman spectrum of CL-C/FeS and commercial FeS are shown in Fig. S1 (a). Two sharp peaks are located at 1334 and 1589 cm⁻¹, which represent the characteristic peaks of carbon materials: the disorder-induced D band and the graphitic G band, respectively [41]. FeS content in the CL-C/FeS microspheres is ca. 76.45 wt% by TG measurement (Fig. S1 (b)). Fig. S2 shows the N₂ adsorption/desorption isotherms of CL-C/FeS. The isotherms present type IV isotherms according to the IUPAC classification, which indicate the mesoporous structure with the specific surface area of 39.49 m² g⁻¹. Based on the BJH calculation, the composite displays a sharp distribution peak centered at 4 nm.

The SEM image in Fig. 2a exhibits that the 3D CL-C/FeS microspheres have the diameter of 10–20 μm . The magnifying SEM image (Fig. 2b) reveals that large amounts of sheet-on-sheet FeS/C nanosheets vertically grow on the center of sphere and assemble together to form a 3D interconnected structure with

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