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Enhancing the reversibility of SnCoS₄ microflower for sodium-ion battery anode material

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ABSTRACT

As the demand of high-performance energy storage devices rises in many applications, sodium-ion batteries have gained widespread researching attention as an alternative of lithium-ion batteries. Because of the high theoretical capacity, SnS₂ received intensive interests. Yet, the undesirable initial Coulombic efficiency and high hysteresis during charge and discharge reactions restrict their possible applications. To circumvent the poor initial Coulombic efficiency of tin sulfide anode materials and prevent the coarsening of Sn nanograins and reduction of the conversion reaction interface between Na₂S and metallic Sn, SnCoS₄ microflower was successfully designed and synthesized as anode material for sodium-ion batteries. The in situ formed Co nanoclusters restrict the coarsening of the materials and promote the sodiation and desodiation reactions, and therefore highly enhance the reversibility and initial Coulombic efficiency. The SnCoS₄ composite shows a highly reversible capacity of 477.76 mA h/g at 100 mA/g with a lower charge-discharge hysteresis.

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1. Introduction

As more and more countries and areas introduce policies and laws to stimulate the consumption of new energy vehicles, battery manufacturing companies and the vehicle companies are working together to develop high-performance energy storage devices to meet the growing demand of new energy vehicle market. Although lithium-ion batteries (LIBs) have commercialized for many years, to make the price of batteries more acceptable and the source more sustainable still remains great challenge [1,2]. Driven by the ample reserve of sodium resources on the earth and cost consideration, sodium-ion batteries (SIBs) gained widespread researching attention as an alternative of lithium-ion batteries [3–6]. However, the obviously larger ion radius of Na⁺ than that of Li⁺ gears down the reaction kinetics and brings about severe volume expansion [7-9].

Two-dimensional (2D) layered metal sulfides, like SnS₂ [10,11], SnS [12,13] and MoS₂ [14–16], rely on the layered structure with a large interlayer spacing accelerating the insertion and extraction of guest ions and accommodating more easily to the volume changes in the host materials during repeated charge and discharge processes. Especially, SnS₂ undergoes multistep reactions with sodium-ions to generate Na₁₅Sn₄ with a high theoretical capacity of 1136 mA h/g. SnS_2 is constituted by a layer of tin atoms sandwiched between two layers of hexagonally close-packed sulfur atoms. The large interlayer spacing (0.5899 nm) contributes to the fast and easy sodium-ion intercalation and diffusion, which could greatly improve the reaction kinetics, and acts as a buffer to adapt to the huge volumetric changes [3,10]. Unfortunately, the 2D layered SnS₂ tends to present the severe stack of adjacent planes by Van Der Waals interaction, which leads to the irreversible capacity loss and short cycle life. More importantly, Sn⁰ metal and Na₂S could just partly convert back to SnS₂ during the desodiation process. The internal stress of recrystallization causes the migration of the intermediate product Sn nanograins, then lead to the aggregation and coarsening of Sn nanograins and reduction of the conversion reaction interface between Na₂S and metallic Sn⁰ [17,18]. The ultimate consequence of coarsening and reduction of conversion reaction interface is a partially reversible conversion reaction and thus an unsatisfying initial Coulombic efficiency (ICE) as well as irreversible capacity loss and structure collapse.







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Many research efforts have been devoted to enhancing the cycle life of SnS₂. For example, Wang et al. reported a freestanding binder-free hierarchical SnS₂ nanoplates decorated on the graphene supported by carbon cloth (SnS₂/graphene/CC) as anode material, in which the graphene acts as the substrate, provides large specific surface area and supports high mass-loading of SnS₂ nanoplates. However, the initial Coulombic efficiency could just reach 52.5%, far away from practical application [19]. It is thereby vital to improve the ICE and reversible capacity of SnS₂.

In 2005, Sony Corporation commercialized a new type of LIB consisting of Sn-Co-C ternary alloys system [20]. Then many researchers have demonstrated that the 3d transition metals, like Co and Fe, could enhance the reversible conversion reaction of SnO₂, attaining high ICE and high reversible capacity of electrode. That is because the intermediate product Co nanoclusters serve as barriers to hinder the migration and coarsening of Sn into large grains during repeated cycling, which greatly boost the reversibility of conversion reaction and restrain the pulverization of structure [21–25]. Liang et al. reported a SnO₂–Co–C ternary composite exhibited high ICE of 80.8%. They revealed the notion that Co additives dramatically inhibit Sn coarsening in the SnO₂-Co-C system by ex situ XRD measurements, and the anode material achieve reversible capacity up to 780 mA h/g at 0.2 A/g after 400 cycles for LIBs [21]. Compared to monometal sulfide, bi-metal sulfide possesses higher electronic conductivity and more abundant redox reactions, which will significantly boost reversible storage of Na⁺ [26 - 29].

Herein, we designed and fabricated a microflower-like SnCoS₄ composite as SIB anode material of enhanced ICE and reversible capacity for the first time. By one-pot solvothermal method, SnCoS₄ composite was fabricated with a 3D microflower structure selfassembled by 2D nanosheets. By designing Sn-Co-S ternary composite, we attained the following goals: (1) The in situ formed Co nanoclusters serve as barriers to hinder the agglomeration and coarsening of Sn, therefore highly improve the area of conversion reaction interface of Na₂S and metallic Sn⁰. Thus, the reversible capacity for the first cycle and initial Coulombic efficiency were greatly promoted to 637.65 mA h/g and 65.3%, respectively, compared to SnS_2 anode of 228.08 mA h/g and 38.5%. (2) The in situ formed Co acts as favorable electron conductor uniformly distributing in the whole microflower and stayed stable since the first charge process, even without any addition of carbonous materials. (3) 3D microflower structure supports the 2D nanosheets to prevent the stack of nanosheets during the repeated cycles and guarantees an enlarged surface area. 2D nanosheets could also offer the benefits of shortened electron and Na⁺ transport distance and enhanced reaction kinetics. As a result, the SnCoS₄ composite showed remarkable reversible capacity of 477.76 mA h/g after 60 cycles at 0.1 A/g, high capacity retention of 75% since the second cycle, and enhanced initial Coulombic efficiency of 65.3% (got a 69.6% enhancement compared to SnS₂ anode).

2. Experimental

2.1. Materials synthesis

All the reactants and solvents were of analytical reagent grade and were used without further purification. The $SnCoS_4$ microflower composite was prepared through a facile one-pot solvothermal approach. Typically, 3 mmol of cobaltous chloride hexahydrate, 3 mmol of tin (IV) chloride pentahydrate, and 12 mmol of L-cysteine were added into 70 mL of ethylene glycol solution under magnetic stirring for 6 h. The obtained solution was then transferred to a 100 mL Teflon tank and sealed in autoclave, which was kept in an oven at 180 °C for 12 h. The resulting precipitate was collected and washed 3 times by centrifugation with de-ionized water and ethanol respectively, after autoclave was naturally cooled down to ambient temperature. Then obtained sample was dried at vacuum drying oven overnight at 60 °C. For contrast, the samples without addition of tin (IV) chloride pentahydrate and cobaltous chloride hexahydrate reagent were prepared, respectively.

2.2. Materials characterization

Scanning electron microscopy (Hitachi SU-70), transmission electron microscopy (Tecnai G2 F30) and high resolution transmission electron microscopy (JEOL JEM-2011) were applied to test the morphology and micro-structure. X-ray diffraction (XRD) experiments of the samples were performed on an X'Pert Pro X-ray diffractometer (PANalytical, the Netherlands) with Cu K α radiation. The XPS spectra were carried out by VG ESCALAB MARK II with a monochromated Al K α X-ray source.

2.3. Electrochemical measurement

The electrochemical tests were performed using CR2025 cointype cells, which were assembled in an argon-filled glove box. The working electrodes were prepared by mixing the as-prepared active materials, acetylene black and sodium alginate under the weight ratio of 70: 15: 15 in DI water. Then the slurry was uniformly coated on the copper foil, last dried in a vacuum oven at 80 °C for overnight. Electrochemical measurements were carried out using two-electrode coin cells with sodium metal as counter and reference electrode. The electrolyte comprised of a solution of 1 M NaClO₄ in ethylene carbonate/diethyl carbonate (1/1; v/v) with 10 wt % fluoroethylene carbonate. Glass microfiber film (GF/D, Whatman) was used as the separator. The cells were galvanostatically charged and discharged at a LAND CT2001A battery tester in the potential range of 0.01–3.00 V (vs. Na/Na⁺) at different constant current densities. Cyclic Voltammetry (CV) measurement was tested by an electrochemical workstation (CHI600E) from 0.01 to 3.00 V (vs. Na/Na⁺) at a scan rate of 0.1 mV/s. Electrochemical impedance spectroscopy measurement was also performed on the same electrochemical workstation over a frequency range between 100 kHz and 0.1 Hz with an amplitude of 5.0 mV.

3. Results and discussion

The morphology of as-prepared SnCoS₄, CoS₂ and SnS₂ samples was characterized by scanning electron microscope (SEM). As shown in Fig. 1a and b, the SnCoS₄ composite shows a uniform flower-like morphology and high monodispersity, with an average size of about 1.0–1.5 µm. As the time of solvothermal prolonged, the nanosheets self-assembled into a microflower. This unique structure could prevent the nanosheet subunit from the agglomeration and stack. The nanosheets display a thickness of about 30 nm. The SnS₂ sample (Fig. 1c and Fig. S1) displays the morphology of curved sheets clustered into a littery paper-ball shape. This evidence illustrate that SnS₂ layer structure tends to agglomerate to reduce its surface area to keep a thermodynamic stability, which would limit the quantity of electrochemical active sites and slower the transport and diffusion of Na⁺. The morphology of CoS₂ sample (Fig. S2) was granular with an average size of 30-50 nm.

The crystal structures of obtained samples were determined by X-ray diffraction (XRD). Fig. 1d shows the XRD pattern of SnCoS₄ microflower, SnCoS₄ sample exhibits four major diffraction peaks centered at 17.07°, 28.74°, 32.67° and 50.86°. The number and the position of diffraction peaks match well with the previous reported



Fig. 1. a–b) SEM images of SnCoS₄ microflower composite, c) SEM images of SnS₂, d) XRD pattern of SnCoS₄ and SnS₂ composite, e) TEM image of SnCoS₄ microflower composite, f) EDS elemental mapping of SnCoS₄ microflower composite: cobalt, tin, sulfur.

work of SnCoS₄/graphene composites [30], which demonstrates the diffraction peaks should be assigned to the pure phase of SnCoS₄. The strong diffraction peaks of the sample without addition of CoCl₂ centered at 28.43°, 32.30°, 41.80°, 50.00°, 52.37°, 58.41° and 60.67° could be indexed to the specific lattice planes of SnS₂ phase (JCPDS card No. 40-1467). Transmission electron microscopy (TEM) was applied to further confirm the microstructure of SnCoS₄ material. As shown in Fig. 1e, the SnCoS₄ displayed a microflower morphology self-assembled by nanosheet subunits, which is consistent with the SEM images. Even though the sample went through ultrasonic treatment when it was prepared, it still exhibits its original morphology, demonstrating the excellent structure stability. From the contrast of TEM image, we could find the 2D layered structure is extremely thin, which could contribute to the fast and easy electrolyte penetration as well as shorten the diffusion distance of electron/ion. High-resolution transmission electron microscopy (HRTEM) was applied to investigate the lattice fringe of SnCoS₄ material. As shown in Fig. S3. The HRTEM image shows high crystallinity of the prepared sample. The parallel atomic planes can

be clearly identified, and the lattice planes with a d-spacing of 0.32 nm and 0.27 nm could be well assigned to $SnCoS_4$ phase [30]. This evidence is clearly verified with the result of XRD pattern. Energy dispersive spectrometer (EDS) was applied to examine the elemental distribution of $SnCoS_4$ composite. As shown in Fig. 1f, the EDS mapping spectra of the $SnCoS_4$ microflower composite illustrates that Co, Sn, S elements are homogeneously distributed within the whole structure.

To investigate the Na⁺ charge and discharge reactions with the SnCoS₄ microflower electrode, SnS₂ electrode and CoS₂ electrode, a cyclic voltammetry (CV) test was performed in the potential range of 0.01–3.0 V (vs. Na⁺/Na) at a scan rate of 0.1 mV/s. CV curves of the SnCoS₄ electrode, SnS₂ electrode and CoS₂ electrode were displayed in Fig. 2(a–c), respectively. For SnCoS₄ electrode (Fig. 2a), in the first cathodic scanning, the peaks at 1.3 V and 1.8 V are attributed to the insertion of sodium-ions into SnCoS₄. The broad reduction peak from 0.5 V to 1.0 V are corresponding to the formation of metallic Sn and Co nanoclusters distributing in Na₂S matrix, and a further sodiation reaction of Sn nanograins on the



Fig. 2. CV curves of the a) SnCoS₄ electrode, b) SnS₂ electrode and c) CoS₂ electrode measured in the potential range of 0.01–3.0 V (vs. Na/Na⁺) at a scan rate of 0.1 mV/s.

interface of Na_2S/Sn^0 [30]. In the first anodic scanning, the peak at 0.07 V and broad peak at 1.2 V are associated with the multi-step dealloying reaction of Na_xSn , the recrystallization of Sn nanograins and the reconversion reaction between metallic Sn and Na_2S [31]. In this stage, Co nanoclusters act as excellent electronic conductors and stabilize the Sn nanograins. Overall cathodic and anodic reactions could be represented as follows:

$$SnCoS_4 + (8+x)Na^+ + (8+x)e \rightarrow Na_xSn + Co + 4Na_2S$$
 (1)

 $NaxSn + 4Na_2S - (x + 8)e^- \leftrightarrow Sn + 4S + (x + 8)Na^+$ (2)

$$Sn + 2Na_2S \leftrightarrow SnS_2 + 4Na^+$$
 (3)

For SnS₂ electrode (Fig. 2b), in the first cathodic curve, a small peak at 1.7 V was ascribed to the intercalation of sodium-ions into the (001) plane [32]. The broad peak at around 0.6 V is attributed to the formation of amorphous Na₂S and metallic Sn nanoparticles, and then further underwent the sodiation process to form Na₁₅Sn₄. During the first anodic sweep, the peaks at 0.07 V and 1.15 V are associated with the multi-step dealloying reaction of Na15Sn4 and the reformation of SnS_2 [10,32,33]. Compared the areas of the first two CV curves, we could observe the large irreversible capacity loss of the initial sodiation/desodiation process. This evidence illustrated a poor ICE of SnS₂ electrode. For CoS₂ electrode (Fig. 2c), in the discharge process, the peaks at 1.25 V should be assigned to insertion of sodium-ions into CoS₂ to form the intermediate product Na_xCoS₂ [34]. In addition, the reduction potentials at 0.57 V match well with potential positions of the displacement reaction of Co and Na₂S. In the anodic curves, the oxidation broad peaks from 1.8 V to 2.1 V correspond to the reverse reaction and recovery of CoS₂ [34–37]. The intermediate product Co plays a role in an electron conductor and inactive metal [38]. The difference between

the first curve and second curve is mainly because the formation of solid electrolyte interphase (SEI) film on the surface of the CoS_2 electrode.

To investigate the function of Co nanoclusters of SnCoS₄ electrode generated in the first discharge process, we conducted the galvanostatic charge-discharge voltage profiles of the SnCoS₄, SnS₂ and CoS₂ electrodes at a current density of 0.1 A/g, in the potential range of 0.01–3.0 V (vs Na/Na⁺). Fig. 3a-c exhibits the galvanostatic charge-discharge voltage profiles of the SnCoS₄, SnS₂ and CoS₂ electrodes, respectively. The galvanostatic charge-discharge voltage curves of SnCoS₄ electrode showed two evident plateaus (Fig. 3a) around at 0.5-1.0 and 1.0-1.5 V, which was consistent with the characteristic voltage position of CV curves. The second and third curves overlapped very well, which indicated the high reversibility of SnCoS₄ electrode. It delivered a high initial discharge capacity of 975.83 mA h/g and reversible capacity of 637.65 mA h/g, with an ICE of 65.3%. The irreversible sodium-ion loss was ascribed to the solid electrolyte interphase (SEI) layer formation in the surface of SnCoS₄ electrode. As shown in Fig. 3b, SnS₂ electrode delivered the first discharge and charge capacities of 591.66 and 228.08 mA h/g, respectively. The ICE value of SnS₂ electrode was only 38.5%. The low ICE of SnS₂ electrode should be attributed to the coarsening of Sn nanograins leading to the irreversibility of conversion reaction. As displayed in Fig. 3c, the first discharge and charge capacities was 630.24 and 338.27 mA h/g, respectively, with an ICE of merely 54.14% for CoS₂ electrode. Compared to SnS₂ anode, SnCoS₄ electrode shows an enhancement of 69.6% in initial Coulombic efficiency. The charge/discharge potential hystereses of SnCoS₄, SnS₂ and CoS₂ electrodes were demonstrated in Fig. 3d. At 50% state of charge/discharge, this potential hysteresis of SnCoS₄ is only 0.49 V, which is substantially lower than 0.7 V for SnS_2 and 1.24 V for CoS_2 , respectively. The ICE of SnCoS₄ electrode is 69.6% higher than that of SnS₂ anode. Especially, when it compares to previously reported



Fig. 3. The galvanostatic charge-discharge voltage profiles of the a) SnCoS₄, b) SnS₂, c) CoS₂ electrodes at a current density of 0.1 A/g, in the potential range of 0.01–3.0 V (vs Na/Na⁺). d) The charge-discharge potential hysteresis of SnCoS₄, SnS₂ and CoS₂ electrodes at a current density of 0.1 A/g.

SnS₂/CC anode with a low ICE of 32.8%, the 2D SnS₂/CNTs electrode with corresponding ICE of 46.7%, and 3D SnS₂/CNTs electrode with ICE of 39.5%, SnCoS₄ electrode achieves a great enhancement [33,39]. The generation of Co nanoclusters could greatly reduce the polarization of electrodes and increase the reversibility of conversion reactions, thus leading to an enhanced initial Coulombic efficiency of anode [40,41]. Galvanostatic intermittent titration technique (GITT) measurements of SnCoS₄ and SnS₂ were exhibited in Figs. S5–S6. The dotted lines represent quasi-equilibrium potentials after fully relaxation for 5 h at open circuit, which are approximately equal to thermodynamic values. At 50% state of discharge, the potential hysteresis of SnCoS₄ (Fig. S5) is only 0.29 V at the current density of 100 mA/g for 0.5 h followed by a 5 h rest, which is much lower than that of SnS₂ (0.41 V) at the current density of 100 mA/g.

Fig. 4a reveals the cycling performances of SnCoS₄, SnS₂ and CoS₂ electrodes at the current density of 100 mA/g. SnCoS₄ electrode delivers a superior electrochemical performance retaining a reversible capacity of 477.76 mA h/g after 60 cycles. Nearly 75% capacity retention was achieved compared to the second cycle. After 60 cycles, SnS₂ electrode displayed reversible capacities of 224.38 mA h/g, and CoS₂ electrode only showed reversible capacities of 83.02 mA h/g, with a poor capacity retention of 24.5%. Although SnS₂ electrode displays a relatively stable cycling performance, its irreversible capacity loss accounts for nearly two thirds of its first discharge capacity. The great enhancement of irreversible capacity and cycling performance of SnCoS₄ electrode was mainly attributed to the follows: 1) The unique 3D flower-like microstructure enlarged the contact area between the electrode and electrolyte, thus exposed plentiful electrochemical active sites, contributing to the improvement of sodium-ion storage capacity. 2) 3D microflowers also played a role in supporting the 2D nanosheets and accommodating more volumetric change during sodiation/ desodiation reactions, which had meaningful contribution to cycling stability. 3) Due to the generation of Co nanoclusters, the reversibility of conversion reactions was successfully increased, providing higher reversible capacity. 4) The synergistic effect of Sn–Co–S bimetal system supplied more abundant redox reactions compared to monometallic sulfide SnS₂.

Fig. 4b reveals the rate capabilities of SnCoS₄, SnS₂ and CoS₂ electrodes at various current densities of 0.05, 0.1, 0.2, 0.5 and 1.0 A/ g for 10 cycles each. For SnCoS₄ anode, a reversible capacity of 687.69 was achieved at 0.05 A/g. When the current densities increased to 0.1, 0.2, 0.5 and 1.0 A/g, the reversible capacities of 623.80, 562.30, 453.96, 347.62 mA h/g were delivered, respectively (Fig. 4b). When the current rate went back to 0.05 A/g, the specific capacity recovered to 616.66 mA h/g. It equals to a capacity retention of 89.67% compared with the initial reversible capacity, which demonstrates an extraordinary rate capability and structural stability of SnCoS₄ anode. SnS₂ and CoS₂ electrodes were also tested under 0.05–1.0 A/g conditions, and they manifested inferior rate capability, delivering specific capacities of 248.41, 229.36, 198.81, 146.82, 104.36 mA h/g and 385.3, 333.33, 272.22, 144.44, 37.76 mA h/g, respectively. Fig. S4 shows the charge/discharge profile at various current densities within 0.01–3.0 V for SnCoS₄.

Electrochemical impedance spectroscopy (EIS) tests were conducted to explore the kinetics performance of $SnCoS_4$ and SnS_2 electrodes reacting with sodium-ions. Fig. 4c shows the Nyquist plots. Every plot consists of a semicircle in the middle frequency area and an inclined line in the low frequency range. The components of the equivalent circuit are exhibited in the inset of Fig. 4c. Charge transfer resistance (R_{ct}) represents ions and electrons transport on the interface of electrolyte and electrode materials. Apparently, owing to the enhanced conductivity of bi-metal sulfide $SnCoS_4$ electrode, the value of R_{ct} is lower than SnS_2 electrode. A lower R_{ct} of the $SnCoS_4$ electrode can also explain its better rate



Fig. 4. a) Cycling performances of SnCoS₄, SnS₂ and CoS₂ electrodes at the current density of 0.1 A/g. b) Rate capabilities of SnCoS₄, SnS₂ and CoS₂ electrodes at current densities of 0.05, 0.1, 0.2, 0.5, 1.0 A/g, respectively. c) The Nyquist plots of the SnCoS₄ and SnS₂ electrodes. d) The relationship lines between Z' vs. ω^{-1/2} in the low frequency range of the SnCoS₄ and SnS₂ electrodes.

capacity compared to other electrodes. The sharper inclined line in the low frequency range of SnCoS₄ is ascribed to the supported 2D nanosheets by the 3D flower-like structure and enlarged surface area, so that the sodium-ion diffusion process could be accelerated. Fig. 4d shows the relationship lines between Z' vs. $\omega^{-1/2}$ in the low frequency range of the SnCoS₄ and SnS₂ electrodes. The sloping line in low frequency indicates the Warburg impedance [39]. The larger Warburg diffusion impedance of SnS₂ electrode than that of SnCoS₄ was attributed to shortened electron/ion transport pathways and facilitated electrolyte penetration of 3D flower-like structure of SnCoS₄. To figure out the sodium-ion diffusion coefficients (D) of three electrodes, we used the following equation:

 $D = R^2 T^2 \ / \ 2n^4 F^4 A^2 C^2 \sigma^2$

Where R is the gas constant, T is room temperature, A is the surface area of the electrode, n is the number of transfer electrons of redox reaction per molecular, F is Faraday's constant, C is the concentration of sodium ions, and σ is the Warburg factor [42,43]. The value of σ of SnCoS₄ and SnS₂ electrodes was calculated, 1122.99 and 1298.59 $\Omega/s^{1/2}$, respectively. Therefore, diffusion coefficients of sodium ion in SnCoS₄ and SnS₂ were 2.57 \times 10⁻¹⁷ cm [2]/s and 1.92 \times 10⁻¹⁷ cm²/s, respectively, which illustrates a faster and easier electrons/ions diffusion on the electrode materials. The kinetic parameters are displayed in Table 1.

Table 1					
Kinetic p	arameters	of SnCoS ₄	electrode	and SnS ₂	electrode.

Electrode	$R_s(\Omega)$	$R_{ct}(\Omega)$	$\sigma(\Omega/s^{1/2})$	D (cm [2]/s)
SnCoS ₄	3.329	63.5	1122.99	$\begin{array}{l} 2.57 \times 10^{-17} \\ 1.92 \times 10^{-17} \end{array}$
SnS ₂	3.172	87.7	1298.59	

The advantages of introducing Sn–Co–S system could be summarized as follows: Tin sulfide provides high specific capacity for the anode. While the generation of Co nanoclusters serve as barriers to hinder the migration and coarsening of Sn into large grains during repeated cycling, therefore greatly reduce the polarization of electrodes and increase the reversibility of conversion reactions, leading to an enhanced initial Coulombic efficiency compared to SnS₂ anode. For another thing, the in situ formed Co acts as favorable electron conductor, so the anode could stay high conductivity even without addition of carbon-based materials.

4. Conclusions

In summary, a unique 3D flower-like SnCoS₄ anode material was successfully synthesized by one-pot solvothermal method. Due to the generation of Co nanoclusters during the first discharge process, the reversibility of conversion reactions was greatly improved. The flower-like SnCoS₄ anode material delivers a high sodium-ion storage reversible capacity of 477.76 mA h/g after 60 cycles with an initial Coulombic efficiency of 65.3%, in which is increased to over 69% compared to the SnS₂ anode. Employing the synergistic effect of bi-metal sulfides for effectively enhancing the initial Coulombic efficiency and reversible capacity of anodes provides promising solutions of exploration for the next generation high-performance SIBs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Jiayi Zhong: Methodology, Data curation, Writing - original draft. Xuezhang Xiao: Methodology, Data curation, Writing original draft, Writing - review & editing. Zunchun Wu: Visualization, Investigation. Nan Zhang: Software, Validation. Ruicheng Jiang: Software, Validation. Xiulin Fan: Writing - review & editing. Lixin Chen: Supervision, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jallcom.2020.154104.

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