



SnSe₂ nanocrystals coupled with hierarchical porous carbon microspheres for long-life sodium ion battery anode

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ABSTRACT Tin selenides have been attracting great attention as anode materials for the state-of-the-art rechargeable sodium-ion batteries (SIBs) due to their high theoretical capacity and low cost. However, they deliver unsatisfactory performance in practice, owing to their intrinsically low conductivity, sluggish kinetics and volume expansion during the charge-discharge process. Herein, we demonstrate the synthesis of SnSe₂ nanocrystals coupled with hierarchical porous carbon (SnSe₂ NCs/C) microspheres for boosting SIBs in terms of capacity, rate ability and durability. The unique structure of SnSe₂ NCs/C possesses several advantages, including inhibiting the agglomeration of SnSe₂ nanoparticles, relieving the volume expansion, accelerating the diffusion kinetics of electrons/ions, enhancing the contact area between the electrode and electrolyte and improving the structural stability of the composite. As a result, the as-obtained SnSe₂ NCs/C microspheres show a high reversible capacity (565 mA h g⁻¹ after 100 cycles at 100 mA g⁻¹), excellent rate capability, and long cycling life stability (363 mA h g⁻¹ at 1 A g⁻¹ after 1000 cycles), which represent the best performances among the reported SIBs based on SnSe₂-based anode materials.

Keywords: tin selenides, nanocrystals, hierarchical, sodium-ion batteries

INTRODUCTION

As a promising alternative to lithium-ion batteries (LIBs), sodium-ion batteries (SIBs) have recently attracted

growing interest particularly for large-scale energy storage applications owing to the abundance and uniform distribution of sodium resource in the earth crust [1–5]. However, their electrochemical performances are severely hindered by severe volume variation and slow kinetics during insertion/extraction processes of sodium ions (Na⁺) due to the intrinsic larger ionic radius and heavier molar mass of sodium ion than lithium ion [6–11]. Particularly, most of anode materials that are suitable for LIBs could not be applied directly in SIBs [12–15]. Therefore, the exploitation of excellent anode materials with high specific capacity, outstanding Na-storage reversibility and excellent rate capability is urgently desirable but remains a challenge.

Recently, Sn-based materials, such as SnO₂ [16–19], SnS [20,21], SnS₂ [22–24], and Sn₃P₄ [25,26], have attracted tremendous attention as promising anode materials for both LIBs and SIBs. As earth-abundant, environmental friendly, and chemically stable materials, tin selenides (including SnSe and SnSe₂) have also been regarded as attractive anode materials for SIBs, yet seldom studied till now [27,28]. SnSe₂ is highlighted due to its unique layered structure and high interlayer spacing (6.14 Å for SnSe₂ vs. the diameter of 1.02 Å for Na⁺), which provides a fast channel for the transfer of ions and electrons [29,30]. Particularly, SnSe₂ as an anode material for SIBs demonstrates a high theoretical reversible capacity of 756 mA h g⁻¹ [31]. However, similar to other Sn-based materials, SnSe₂ is known for several drawbacks including

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the low electrical conductivity, huge volume variation and high mechanical stress/strain upon cycling, inevitably resulting in serious kinetic problems, making it difficult to fully take advantage of the conversion reactions, and thus leading to limited reversible capacity, cycle stability, and rate capability in practical application [29–32].

To solve these issues, herein, we report a facile strategy to prepare SnSe₂ nanocrystals coupled with hierarchical porous carbon (SnSe₂ NCs/C) microspheres. First, uniform stanniferous solid precursor microspheres were synthesized by a one-pot solvent-thermal method in the presence of stannous chloride and ascorbic acid in a mixed isopropanol/glycerol solution, which were subsequently transferred into SnO₂ NCs/C microspheres by the thermal treatment in Ar. Then, the as-prepared SnO₂ NCs/C microspheres underwent a simple selenization reaction to form SnSe₂ NCs/C microspheres, which were particularly attractive for solving the problems related to SIBs. The SnSe₂ NCs/C microspheres inhibits the agglomeration of SnSe₂ nanocrystals by separating them from each other, and greatly improves the conductivity as well as availability of electrode materials. The 3D hierarchical porous structure not only enhances the contact

area between the electrode and electrolyte, but also helps to suppress the volume expansion during charge-discharge processes. The SnSe₂ nanocrystals are small and uniformly anchor on the carbon networks, and thus accelerate the diffusion kinetics of electrons/ions and improve the stability of the structure. Benefiting from these structural advantages, the SIBs based on the as-prepared SnSe₂ NCs/C microspheres exhibit a high reversible specific capacity of 565 mA h g⁻¹ at 100 mA g⁻¹, an excellent cycling stability (363 mA h g⁻¹ at 1 A g⁻¹ after 1000 cycles), and superior rate capability.

RESULTS AND DISCUSSION

Morphological and structural characterization

The design and synthetic process of the SnSe₂ NCs/C microspheres is schematically illustrated in Fig. 1a. Firstly, Sn-precursor (Sn-P) microspheres were facilely prepared by a one-pot solvent-thermal method in the presence of stannous chloride and ascorbic acid in a mixed isopropanol/glycerol solution. Subsequently, the uniform SnO₂ NCs/C microspheres were formed by annealing those Sn-precursor microspheres in Ar. Finally,

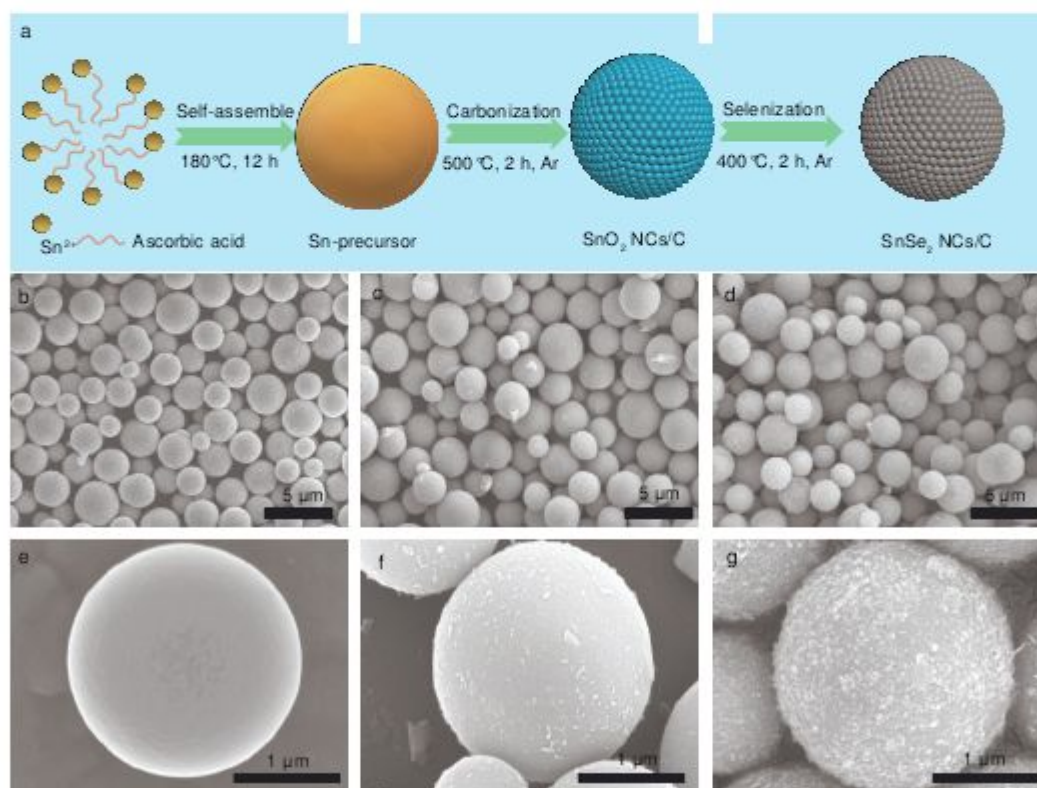


Figure 1 (a) Schematic illustration of the formation process of SnSe₂ NCs/C microspheres. SEM images of the as-synthesized Sn-precursor microspheres (b, e); SnO₂ NCs/C microspheres (c, f) and SnSe₂ NCs/C microspheres (d, g).

the SnSe₂ NCs/C microspheres were obtained *via* simple selenization in Ar atmosphere.

The morphologies of the as-synthesized Sn-P microspheres, SnO₂ NCs/C microspheres, and SnSe₂ NCs/C microspheres were investigated with the scanning electron microscope (SEM) as shown in Fig. 1b–g. In Fig. 1b, e, the Sn-P particles have a size of ~2 μm with an ideal microsphere morphology. After the annealing treatment in Ar, the Sn-P microspheres are transformed to SnO₂ NCs/C microspheres, with the morphology and particle size unchanged (Fig. 1c, f). These SnO₂ NCs/C microspheres exhibit the hierarchical structure consisting of primary nanoparticles. After the selenization, the SnSe₂ NCs/C microspheres still retain the spherical morphology (Fig. 1d, g). Fig. 2a shows a typical SnSe₂ NCs/C microsphere with the corresponding energy dispersive X-ray spectrum (EDS) elemental mapping shown in Fig. 2b. The atomic ratio of Sn/Se is about 1:2, confirming the chemical composition of SnSe₂ NCs/C. All of the expected elements of the composite can be recognized. Transmission electron microscopy (TEM) and high-re-

solution TEM (HRTEM) were carried out to further investigate the microstructure of the SnSe₂ NCs/C. As shown in Fig. 2c, the SnSe₂ NCs/C microspheres have a diameter of approximately 2 μm, in accordance with the SEM results. A highly porous hollow interior structure densely dispersed with small nanoparticles (SnSe₂) can be confirmed by the non-uniform contrast. The HRTEM image in Fig. 2d shows that the SnSe₂ NCs with the size of nanometers (~10 nm) are embedded in the carbon matrix. The clear lattice fringes indicate their good crystallinity. The resolved lattice fringes of these SnSe₂ NCs with an interplanar spacing of 0.29 nm correspond to (101) crystal facets of SnSe₂. The compact and robust SnSe₂ NCs/C microspheres assembled by spherical nanoparticles are able to increase the contact area between the electrode and electrolyte, relieve the volume expansion during the insertion/extraction of Na⁺, and accelerate the diffusion kinetics of Na-ion due to the shortened Na diffusion distances.

The crystal structures of the as-synthesized Sn-P microspheres, SnO₂ NCs/C microspheres, and SnSe₂ NCs/C

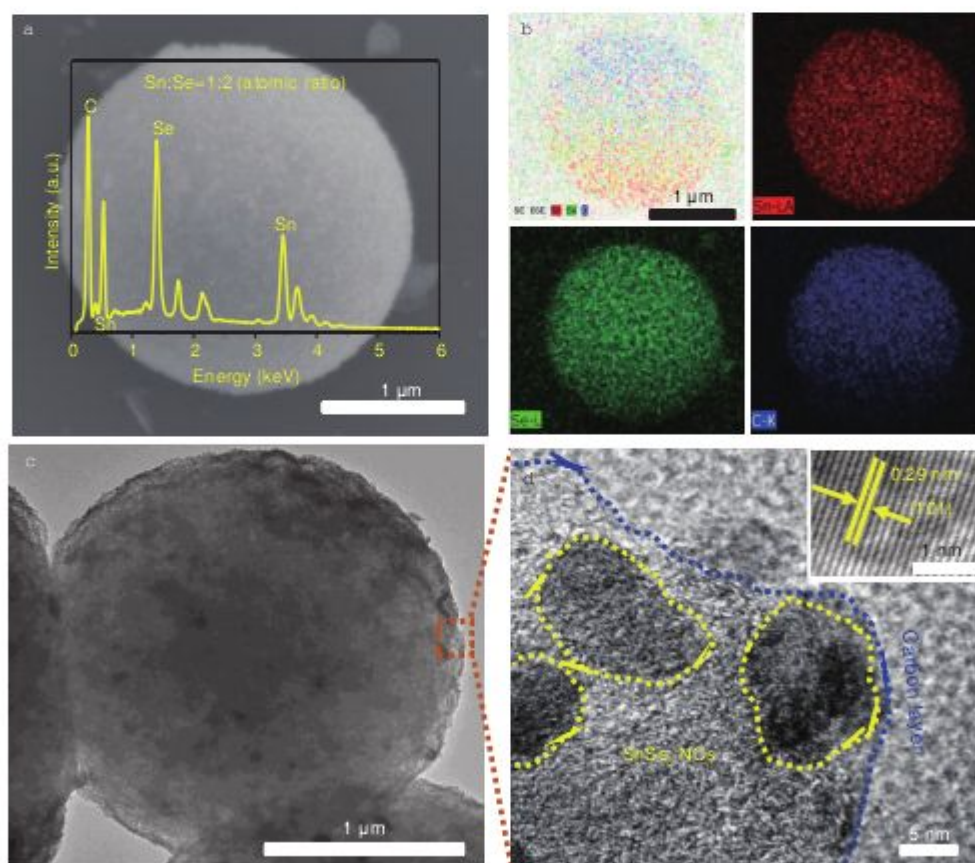


Figure 2 (a) Typical SEM image of SnSe₂ NCs/C microspheres and the corresponding elemental mapping of (b) tin, selenium, and carbon elements. (c) TEM and (d) HRTEM images of SnSe₂ NCs/C.

microspheres were characterized by the powder X-ray diffraction (PXRD) (Fig. 3a), showing the Sn-P microspheres with low crystallinity. After annealing in Ar at 500°C for 2 h, the as-prepared Sn-P microspheres can be converted to SnO₂ (JCPDS No. 41-1445). In addition, for the PXRD of final products, all Bragg peaks can be indexed to the hexagonal phase SnSe₂ (JCPDS No. 23-0602), suggesting that the SnO₂ is completely converted into the phase-pure SnSe₂ via the thermal selenization. Furthermore, no significant carbon diffraction peaks are observed, suggesting its amorphous state. Fig. S1 presents the hexagonal layered crystal structure of SnSe₂. The specific surface area (SSA) of the SnSe₂ NCs/C microspheres was further characterized with the Brunauer-

Emmett-Teller (BET) analysis (Fig. 3b). The SnSe₂ NCs/C possesses a large SSA of 73.9 m² g⁻¹ and a high pore volume of 0.068 cm³ g⁻¹, in good agreement with TEM and HRTEM results. The SnSe₂ NCs/C with large SSA is beneficial to increasing the contact area between the electrode and electrolyte, improving electrolyte transfer and carrier transport kinetics, and thus boosting the performance of SIBs. The amorphous carbon content in the SnSe₂ NCs/C is about 15 wt%, as measured by inductively coupled plasma mass spectrometry (ICP). As control experiment, the bulk SnSe₂ was synthesized by annealing Sn with Se powder in Ar at 500°C for 2 h, and characterized with the PXRD (Fig. S2) and SEM (Fig. S3).

In order to further investigate the chemical composi-

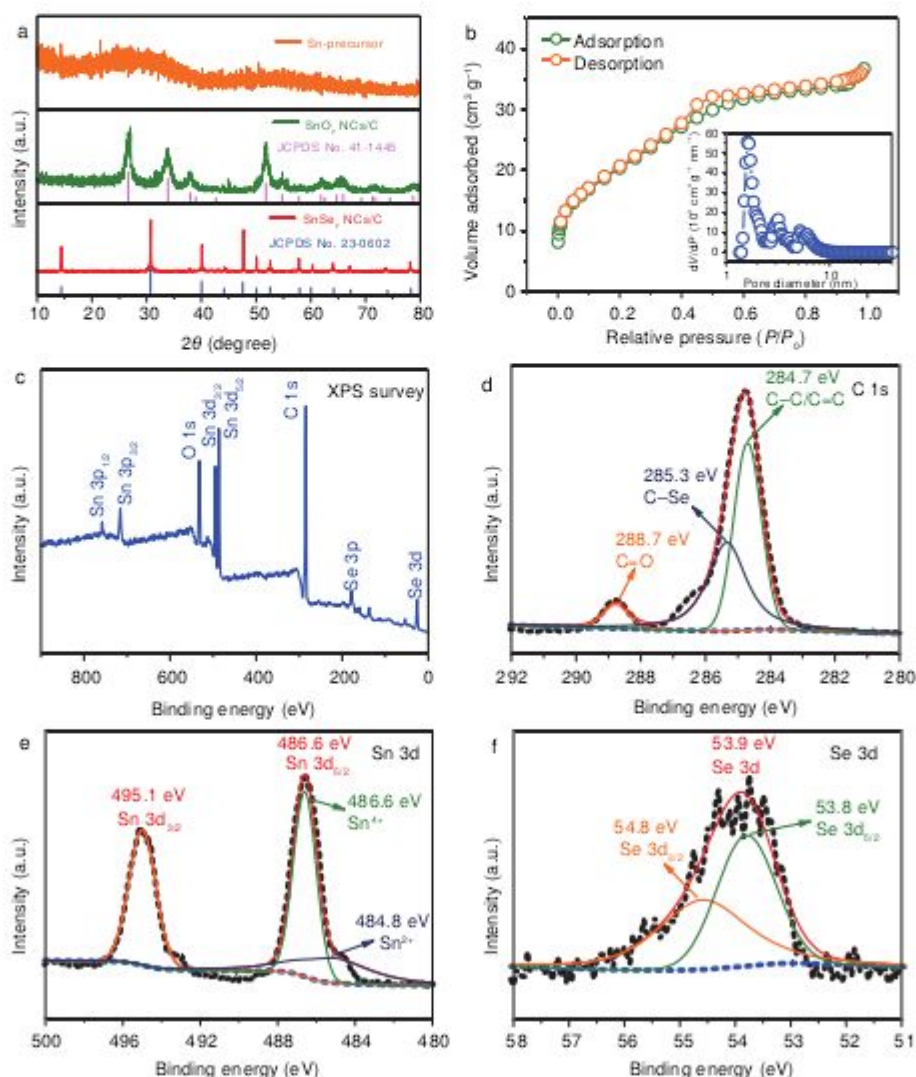


Figure 3 (a) PXRD patterns of the as-synthesized Sn-precursor, SnO₂ NCs/C, and SnSe₂ NCs/C microspheres. (b) Nitrogen adsorption-desorption isotherms and pore size distribution (the inset) of SnSe₂ NCs/C microspheres. XPS spectra of the SnSe₂ NCs/C microspheres survey (c), C 1s (d), Sn 3d (e), and Se 3d (f).

tion and states of the elements on the surface of SnSe₂ NCs/C, X-ray photoelectron spectroscopy (XPS) was carried out (Fig. 3c–f). The survey spectrum demonstrates the presence of Sn, Se, and C in the SnSe₂ NCs/C (Fig. 3c). The high resolution C 1s spectrum in Fig. 3d shows three peaks at 284.7, 285.3, and 288.7 eV, corresponding to sp²-hybridized C, –C–Se, and C=O, respectively [29]. As shown in Fig. 3e, the peaks located at 486.6 and 495.1 eV can be assigned to Sn 3d_{5/2} and Sn 3d_{3/2}, respectively. In accordance with the fitting results, Sn²⁺ valence state (484.8 eV) only occupies for a very small portion compared with the intense peak of Sn⁴⁺ valence state at 486.6 eV, suggesting that Sn⁴⁺ rather than Sn²⁺ is the predominant form of Sn in the as-prepared sample [33]. In addition, the binding energies of 53.9 and 54.8 eV correspond well with Se 3d_{5/2} and Se 3d_{3/2} (Fig. 3f),

confirming the oxidation state of Se²⁻ [34].

Electrochemical characterization

The electrochemical performance of the SnSe₂ NCs/C sample was investigated in 2032 coin cells *via* assembling the electrode into sodium half-cell. Fig. 4a presents the initial five cyclic voltammogram (CV) curves of the SnSe₂ NCs/C composite in the voltage range of 0.01–3.0 V (*vs.* Na⁺/Na) at the scan rate of 0.1 mV s⁻¹. In the initial cathodic sweep, three strong peaks at 1.67, 1.36 and 0.98 V, which disappear in the following four cycles, can be attributed to the initial insertion of sodium ion in SnSe₂ interlayers with the formation of Na_xSnSe₂ (Equation (1)), similar to the lithium and sodium insertion of SnS₂ layer [35,36]. The sharp peak at 0.67 V in the first cycle decreases in the second cycle, which is caused by the

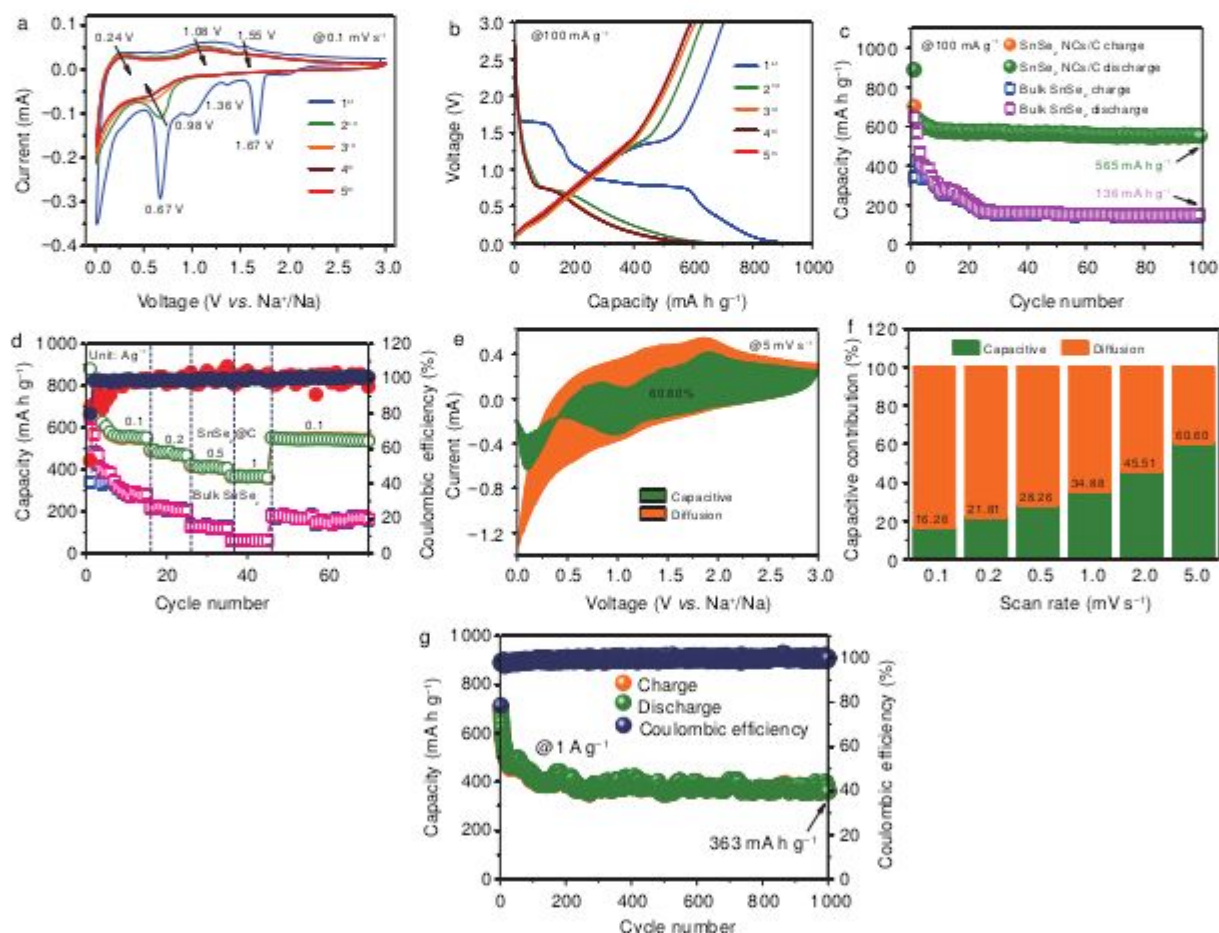
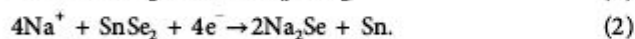
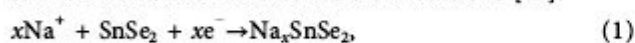


Figure 4 (a) CV curves of the SnSe₂ NCs/C in the first five cycles at a scan rate of 0.1 mV s⁻¹. (b) Charge-discharge profiles for the SnSe₂ NCs/C at 100 mA g⁻¹ in the first five cycles. (c) Cycling performances of the SnSe₂ NCs/C and bulk SnSe₂ at 100 mA g⁻¹ for 100 cycles. (d) Rate performances of the SnSe₂ NCs/C and bulk SnSe₂ at various current densities from 0.1 to 1 A g⁻¹. (e) CV curve with the pseudocapacitive contribution shown in the olive region at a scan rate of 5 mV s⁻¹. (f) The bar chart shows the contribution ratios of capacitive capacity and diffusion-limited capacity at various scan rates. (g) Long-term cycle performance of SnSe₂ NCs/C at 1 A g⁻¹ for 1000 cycles.

reduction of SnSe₂ to metallic Sn, the formation of Na₂Se, and the formation of irreversible solid electrolyte interphase (SEI) layer (Equation (2)) [37,38]. During the initial anodic sweep, the broad peaks at near 0.24 and 1.08 V are attributed to the conversion process from metallic Sn to Na_{3.75}Sn (Equation (3)), while the peak at 1.55 V is related to the restitution process with the formation of SnSe₂ [29,39]. Furthermore, the overlapping CV curves between the fourth and fifth cycles suggest the potentially excellent cycling capability of SnSe₂ NCs/C.

Based on the previous reports on the SnSe₂ anode for Na storage, the initial charging process can be attributed to the intercalation and conversion reactions [29]:



The subsequent charging/discharging cycles were characterized by reversibly alloying and de-alloying Sn and Na_{3.75}Sn [29]:

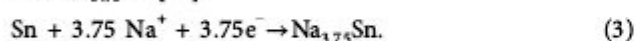


Fig. 4b shows the typical galvanostatic charge-discharge profiles of the SnSe₂ NCs/C electrode for the first five cycles in the voltage range of 0.01–3.0 V at a current density of 100 mA g⁻¹. The charge-discharge voltage plateaus, corresponding to the different stage phase transformations, can be well distinguished, in good agreement with the CV results. For instance, the initial discharge voltage plateau located at 1.67 V, which disappears in the following cycles, is ascribed to the irreversible intercalation of sodium ions into SnSe₂ interlayers. In addition, the broad plateaus at 0.45–0.95 V (for the discharge process) and 0.85–1.55 V (for the charging process) represent the contribution from the reversible sodium ion insertion/extraction.

The first discharge and charge steps deliver specific capacity values of 885 and 702 mA h g⁻¹, respectively, corresponding to a high initial coulombic efficiency (CE) of 79%, and the capacity loss is considered to be caused by the formation of irreversible SEI film on the surface of the electrode and the decomposition of electrolyte. Furthermore, the charge-discharge curves nearly overlap with each other except for the first two cycles, which indicates the high reversibility of the SnSe₂ NCs/C as an anode material for SIBs. One most impressive feature of the SnSe₂ NCs/C electrode is the cyclicity. As shown in Fig. 4c, the SnSe₂ NCs/C electrode achieves a stable capacity of 565 mA h g⁻¹ after 100 cycles at a current density of 100 mA g⁻¹, accounting for 96.4% of the capacity of the 7th cycle, while the bulk SnSe₂ electrode only retains a capacity of 136 mA g⁻¹. These results indicate that the

anode materials with high conductivity and low volume change are favored to enhance the cycle performance and reversible capacity of SIBs. Fig. S4 shows the electrochemical impedance spectroscopy (EIS) measurements of the bulk SnSe₂ and SnSe₂ NCs/C anode at open circuit voltage and after the 20th cycle. It is shown that the diameter of the semicircle for SnSe₂ NCs/C anode is much smaller than that of the bulk SnSe₂ anode in SIBs after the 20th cycle, suggesting lower charge-transfer resistance (*R_{ct}*), which can be ascribed to the good conductivity and stable electrode/electrolyte interface.

High rate capacity is a key parameter to assess the electrochemical performance of electrode materials, and the SnSe₂ NCs/C electrode exhibits a robust rate capability. As shown in Fig. 4d, the SnSe₂ NCs/C demonstrates a capacity of 548 mA h g⁻¹ at a galvanostatic rate of 0.1 A g⁻¹, and 472, 414, and 366 mA h g⁻¹ at rates of 0.2, 0.5, and 1 A g⁻¹, respectively. Moreover, when the current density is restored to 0.1 A g⁻¹, the reversible capacity can revert to 536 mA h g⁻¹, indicating the good reversibility. However, the rate performance of the bulk SnSe₂ anode was inferior, only showing the capacities of 281, 206, 121, and 62 mA h g⁻¹ under rates of 0.1, 0.2, 0.5, and 1 A g⁻¹, respectively. When the current density was set back to 0.1 A g⁻¹, only a reversible capacity of 167 mA h g⁻¹ was preserved. Compared with the bulk SnSe₂ electrode, the SnSe₂ NC/C composite electrodes demonstrate a high reversible specific capacity and an excellent cyclic performance (Fig. 4c), which can be attributed to the following aspects: (1) the SnSe₂ NCs/C microspheres inhibit the agglomeration of SnSe₂ nanocrystals by separating them from each other, and also greatly improve the conductivity as well as availability of electrode materials. (2) The 3D hierarchical porous structure not only enhances the contact area between the electrode and electrolyte, but also helps to suppress the volume expansion during the charge-discharge processes. (3) The SnSe₂ nanocrystals are small and uniformly anchor on the carbon networks, and thus accelerate the diffusion kinetics of electrons/ions and improve its structural stability.

In order to investigate the reason why the SnSe₂ NCs/C electrode has such an excellent rate capability, the charge storage behavior and reaction kinetics were conducted by correlating the currents (*i*) with sweep rate (*v*) based on Equation (4) [40]:

$$i = av^b, \quad (4)$$

where *b* reflects the charge storage behavior, as shown in Fig. S5. Typically, *b* indicates the diffusion controlled process (battery behavior), and the *b* value of 1.0 means

the surface capacitance controlled process (capacitor behavior). Fig. S6 shows the linear relationships between $\log(i)$ and $\log(v)$. The b values of the anodic peak of SnSe₂ NCs/C is 0.86, indicating that Na-ion storage is mainly controlled by surface capacitance in the discharge process. The b values of the three cathodic peaks of SnSe₂ NCs/C are calculated to be 0.65, 0.62, and 0.75, implying the diffusion and surface capacitance controlled behavior coexisted in the charge process. To further quantify the storage contribution for SnSe₂ NCs/C, the current (i) was separated at a fixed voltage (V) based on the following equation [41–53]:

$$i(V) = k_1 v + k_2 v^{1/2}, \quad (5)$$

where $k_1 v$ stands for the capacitive contribution, whereas $k_2 v^{1/2}$ represents the diffusion-controlled contribution, and the constants k_1 and k_2 are obtained from the linear plots of $i(V)/v^{1/2}$ vs. $v^{1/2}$ at a certain voltage. As shown in Fig. 4e, the capacitive capacity contribution to the total charge for SnSe₂ NCs/C electrode is 60.6% at a scan rate of 5 mV s⁻¹. Moreover, the capacitive contribution in CV curve at other scan rates is shown in Fig. S7. Fig. 4f shows the corresponding bar chart of the contribution ratios of capacitive behavior at various scan rates, which reveals that the capacitive contribution dominates gradually with the increase of scan rate, suggesting the noticeable enhancement in the rate performance of the SnSe₂ NCs/C electrode. As shown in Fig. 4g, the SnSe₂ NCs/C electrode exhibits excellent long-term cycling performance, retaining a capacity of 363 mA h g⁻¹ over 1000 cycles at a high current density of 1 A g⁻¹, which represents the best superior cycle stability in all the reported tin selenides based anode materials for SIBs (Table S1).

CONCLUSION

In summary, SnSe₂ nanocrystals coupled with hierarchical porous carbon microspheres can be used as a remarkable anode material for SIBs. The unusual structural and compositional features of the as-obtained SnSe₂ NCs/C can inhibit the agglomeration of SnSe₂ nanoparticles, relieve the volume expansion, accelerate the diffusion kinetics of electrons/ions, enhance the contact area between the electrode and electrolyte, and improve the structural stability of the composite. The SIBs with SnSe₂ NCs/C microspheres as anode materials show superior electrochemical properties (565 mA h g⁻¹ after 100 cycles at 100 mA g⁻¹), excellent rate capability, and ultralong cycling stability (363 mA h g⁻¹ at 1 A g⁻¹ after 1000 cycles). This study provides valuable guidance for rationally developing advanced electrode materials for high per-

formance SIBs.

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Supplementary information Experimental details and supporting data are available in the online version of the paper.



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SnSe₂纳米晶耦合分层多孔碳微球作为长寿命钠离子电池负极材料

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摘要 硒化锡用于钠离子电池负极时具有较高的理论比容量且其成本低廉,因而备受关注.然而,由于其固有的低导电性,以及在充放电过程中的缓慢动力学和体积膨胀,硒化锡作为钠离子电池负极材料表现出的性能较差.本文首次合成SnSe₂纳米晶耦合分层多孔碳微球(SnSe₂ NCs/C)用于增强钠离子电池的比容量、倍率能力和持久性. SnSe₂ NCs/C独特的结构可以有效阻止SnSe₂纳米晶的团聚,减轻材料体积膨胀,加快电子和离子的扩散,增大电解液与电极材料的接触面积,提高材料结构的稳定性.所制备的SnSe₂ NCs/C微球具有较高的可逆比容量(在100 mA g⁻¹的电流密度下循环100圈后仍保持565 mA h g⁻¹的比容量),出色的倍率能力和长循环寿命稳定性(在1 A g⁻¹的电流密度下循环1000圈后仍保持363 mA h g⁻¹的比容量).