Sn-C bonding riveted SnSe nanoplates vertically grown on nitrogen-doped carbon nanobelts for high-performance sodium-ion battery anodes

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SnSe is a promising anode material in sodium-ion batteries (SIBs) due to its high theoretical capacity (780 mAh g\(^{-1}\)) and natural abundance. Herein, we report SnSe nanoplates vertically grown on nitrogen-doped carbon (SnSe/NC) with strong Sn-C bonding for high-performance anode in SIBs, which are synthesized by a facial cation-exchange strategy. The vertically grown SnSe nanoplates with large interplanar spacing (0.58 nm), strong electronic coupling of Sn-C bonding between SnSe and NC facilitate the fast electron/ion transfer, enabling high pseudocapacitive Na-ion storage and enhanced power capability. Density functional theory calculations demonstrate that the presence of N heteroatoms in NC matrix has a pivotal influence on the formation of Sn-C bonding to stabilize the SnSe/NC structure. Moreover, the SnSe nanoplates of SnSe/NC exhibits low interlayer Na\(^+\) diffusion barrier (0.1 eV) and low energy barrier (0.14 eV/uc) from discharged product to pristine SnSe/NC, implying the fast Na\(^+\) diffusion capability and good reversibility. Consequently, the SnSe/NC exhibits large capacities of 723 and 88 mA h g\(^{-1}\) at 0.025 and 20 A g\(^{-1}\), respectively, and 82% capacity retention for over 200 cycles at 2 A g\(^{-1}\), boosting promising applications in high-performance SIBs.

1. Introduction

Sodium-ion batteries (SIBs) have attracted increasing attention as an alternative to lithium-ion batteries (LIBs) for large-scale energy storage because of the low cost and more Na resources, but it is challenging to design and prepare the suitable anode materials for SIBs [1–3]. Commercial graphite anode materials for LIBs have been shown to have low electrochemical activity for Na-ion storage due to the larger ionic radius of Na\(^+\) than Li\(^+\) (1.02 Å vs 0.76 Å in radius) [4]. Although hard carbon materials have been reported to have a high reversible capacity of 300 mAh g\(^{-1}\), the low Na-ion insertion plateau below 0.1 V (vs Na\(^+\)/Na) and low initial cycling coulombic efficiency (CE) pose serious issues in practical applications [5,6].

Two-dimensional (2D) layered metal sulfides and selenides have recently been studied extensively for high-energy-density SIBs due to their layered structures and high theoretical capacities. Among them, 2D tin selenide (SnSe) is particularly promising because of its high theoretical capacity (780 mA h g\(^{-1}\)), good natural abundance and the narrow band gap (0.9 eV) [7]. Zhang et al. reported that SnSe nanosheet clusters had a Na-ion capacity of 738 mA h g\(^{-1}\) at 25 mA g\(^{-1}\) and about 60% capacity retention after 100 cycles at 2 A g\(^{-1}\) [8]. Guo et al. prepared SnSe nanoplates by a colloidal technique in an oil bath, which showed a reversible Na-ion storage capacity of 463.6 mA h g\(^{-1}\) at 0.05 A g\(^{-1}\) [9]. Despite great progress, the large volume change and sluggish sodiation kinetics of SnSe during the discharge/charge process result in undesirable cycling performance and poor output power. To ameliorate the structural stability and electrical conductivity of SnSe-based anodes, hybrid SnSe nanocomposites with conductive carbonaceous materials such as carbon fibers, graphene, and carbon nanotubes have been generally employed as anodes in SIBs [7]. However, the 2D SnSe nanoplates are normally random orientation and distribution with a stacked geometry giving rise to congested Na\(^+\) diffusion channels. Moreover, the weak interface electric/chemical coupling between SnSe and carbon still hinder a larger charge-transfer barrier and voltage...

hysteresis during the sodiation/desodiation process. As a result, the SnSe/carbon composites generally deliver unsatisfactory electrochemical kinetics. To achieve the enhanced redox kinetics and power density, it is desirable to prepare vertically grown SnSe nanoplates on the carbon matrix with the strong interface coupling between SnSe and carbon, so that Na\(^+\) can diffuse easily between the SnSe layers and electrons can traverse rapidly from the carbon matrix to SnSe.

Herein, we report the Sn-C bonding riveted SnSe nanoplates vertically grown on nitrogen-doped carbon (SnSe/NC) nanobelts for high-performance anode in SIBs, which are prepared via a cation-exchange synthesis from carbonized ZnSe-amine hybrid nanobelts (ZnSe/NC) for the first time. The vertical SnSe nanoplates with a large interlayer spacing and open structure provide fast Na\(^+\) diffusion channels. In addition, the conductive NC layers effectively limit the aggregation of SnSe during cycling and improve the electrical conductivity of the composite. More importantly, the strong interfacial interaction between SnSe and NC via the Sn-C bonding significantly enhances the charge transfer and structural stability of the SnSe/NC electrode. Thus, the novel riveted structure of SnSe/NC nanobelts exhibit enhanced pseudocapacitive Na-ion storage through the fast and efficient Faradaic redox reactions at SnSe (sub)surface. Density functional theory (DFT) calculations demonstrate that the presence of N heteroatom in NC matrix displays an important effect on the formation of Sn-C bonding to stabilize the SnSe/NC structure. SnSe of SnSe/NC exhibits an extremely low interlayer Na\(^+\) diffusion barrier of 0.1 eV from the result of DFT calculation, which is much smaller than those of MoS\(_2\) [10], SnO\(_2\) [11], Sb\(_2\)S\(_3\) [12], and black P [13], and even lower than Li\(^+\) diffusion barrier in bilayer MoS\(_2\) [31], Li\(_2\)V\(_4\)O\(_8\) [32], ReS\(_2\) [33], and graphite [34]. Moreover, the energy barrier from the discharged product (Sn) to pristine SnSe/NC is calculated to be 0.14 eV/uc, easy to occur at the cathode. The energy barrier from the discharged product (Sn) to pristine SnSe/NC is calculated to be 0.14 eV/uc, easy to occur at the cathode.

The structure, composition, and morphology of the samples were investigated by X-ray diffraction (XRD, Philips XPert Pro) with Cu K\(_{\alpha}\) radiation, field-emission scanning electron microscopy (FESEM, FEI Nano-SEM 450), transmission electron microscopy (TEM, FEI Titan 60–300 Cs), high-resolution TEM (HR-TEM, Tecnai G20), Raman scattering (HR RamLab), and X-ray photoelectron spectroscopy (XPS, ESCALB MK-II). The NC content in the SnSe/NC was determined by thermogravimetric analysis (TGA, NETZSCH; TG 209 F3) in air using a heating rate of 10 °C min\(^{-1}\). The nitrogen adsorption and desorption isotherms were determined by the Brunauer-Emmett-Teller (BET, Micrometrics, ASAP2010) method.

2.1.2. Preparation of hierarchical SnSe/NC nanobelts

In the typical process, the ZnSe/NC nanobelts (60 mg) were dispersed in 35 mL of deionized water and 1.2 mmol SnSO\(_4\) was added to the solution and stirring for 20 min. The dispersion was transferred into 50 mL Teflon-lined stainless-steel autoclave, kept at 120 °C for 6 h, and cooled naturally. The black powder was collected by filtration and dried at 60 °C under vacuum. For comparison, the pure SnSe nanobelts were prepared by a similar method with ZnSe(DETA)$_{0.5}$ nanobelts as precursor, while the cation-exchange reaction parameters were the same.

2.2. Materials characterization

The electrochemical characterizations were evaluated using two-electrode coin cells with Na metal serving as both the reference electrode and counter electrode. The working electrodes were prepared by mixing 70 wt% of the active materials (SnSe/NC), 20 wt% of acetylene black, and 10 wt% of carboxyl methyl cellulose in deionized water. The slurry was spread uniformly on a copper foil and vacuum dried at 80 °C for 6 h, and then punched into disks. The loading of the active materials was about 1.5 mg cm\(^{-2}\). The coin cells (CR2023) were assembled in an argon filled glovebox with glass fiber filters (Whatman GF/C) as the separator and 1 m NaClO\(_4\) with ethylene carbonate (EC), diethylene carbonate (DEC), and 5% fluoroethylene carbonate (FEC) as the electrolyte. Galvanostatic charging-discharging tests were conducted on the MTP automatic battery cyclers in a potential range between 0.001 and 3.0 V and cyclic voltammetry (CV) was performed on the CHI 760D electrochemical workstation. Electrochemical impedance spectroscopy (EIS) was carried out on the Autolab Electrochemical workstation in a frequency range between 0.1 MHz and 0.1 Hz with a perturbation amplitude of 5 mV.

2.4. DFT calculations

DFT calculations were performed with the plane-wave package PWmat [15,16]. GGA exchange-correlation functional was used to relax the atomic structure and compute the electronic properties. The norm-converging pseudopotential was used with a wave function energy cutoff of 50 Ryd. The atomic coordinates were fully relaxed until the maximal force on each atom was less than 0.05 eV/Å. The k-point meshes were set of 1 × 1 × 1, 5 × 5 × 1, 9 × 9 × 1 for geometry optimization, electronic self-consistent, and density of states (DOS) calculation, respectively. All constructions possess larger than 10 Å vacuum region to minimize the interactions between adjacent image cells.

3. Results and discussion

Fig. 1A schematically illustrates the procedures to prepare the SnSe/NC nanobelts. The lamellar inorganic-organic hybrid ZnSe(DETA)$_{0.5}$ ([ZnSe](Diethylenetriamine)$_{0.5}$) nanobelts are first fabricated hydrothermally on a large scale and then converted into SnSe/NC nanobelts by the carbonization of the interlayered DETA molecules (Fig. 1A, Step 1). The SnSe/NC nanobelts are produced via a cation-exchange reaction of ZnSe/NC in the SnSO\(_4\) solution. Since SnSe has a smaller solubility constant (K\(_{sp}\) = 3.98 × 10\(^{-39}\)) than ZnSe (K\(_{sp}\) = 3.6 × 10\(^{-36}\)), Zn (II) ions in the ZnSe/NC nanobelts are replaced by Sn (II) ions in the SnSO\(_4\) solution and the in situ formed SnSe species nucleate and grow vertically on the NC layer to form the SnSe/NC nanobelts (Fig. 1A, Step 2). The as-fabricated ZnSe(DETA)$_{0.5}$ nanobelts show a width of 300–500 nm and length of 2–5 μm (Fig. 1B, Fig. S1). The X-ray
diffraction pattern (XRD) of ZnSe(DETA)$_{0.5}$ is consistent with the previous reports (Fig. S2) [14,17]. After annealing at 650 °C under Ar, the interlayered DETA molecules are carbonized into NC and the ZnSe/NC nanobelts are formed. Field-emission scanning electron microscopy (FE-SEM) reveals that the ZnSe/NC nanobelts (Fig. 1C, Fig. S3A) inherit the nanobelt morphology of ZnSe(DETA)$_{0.5}$. However, the TEM image discloses the wrinkled surface of ZnSe/NC nanobelts (Fig. S3B), which may arise from the local stress change by the carbonization of SnSe/NC hybrid nanobelts.

Fig. 1. (A) Schematic illustration of the preparation process of SnSe/NC hybrid nanobelts and the SEM images of (B) ZnSe(DETA)$_{0.5}$, (C) ZnSe/NC, and (D) SnSe/NC nanobelts.

Fig. 2. (A) XRD pattern, (B) TEM image, (C) High-magnification TEM image, (D) HR-TEM image, (E) HAADF-STEM image and corresponding elemental maps of SnSe/NC. Inset in (C) is the thickness distribution histogram of the SnSe nanoplates on SnSe/NC.
interlayered DETA molecules [17,18]. The corresponding XRD patterns can be indexed to hexagonal ZnSe (JCPDS 15–0105) and no SnSe (DETA)0.5 diffraction peaks are observed (Fig. S2). Raman scattering confirms the presence of N-doped carbon in the ZnSe/NC nanobelts (Fig. S4). The high-resolution transmission electron microscopy (HR-TEM) image shows a spacing of 0.34 nm corresponding to the (100) plane of hexagonal ZnSe (Fig. S3C). The elemental maps of ZnSe/NC nanobelts show the uniform distribution of Sn, Zn, Se, and C, and N elements throughout the nanobelts (Fig. S3D). The SEM image of SnSe/NC is depicted in Fig. 1D, disclosing that SnSe/NC retains the nanobelts morphology but have many vertical nanofilaments on the surface.

Fig. 2A shows the XRD pattern of SnSe/NC and the peaks can be indexed into the orthorhombic phase of SnSe (JCPDS Card no. 89–0232) and no other impurity such as SnSe2 can be observed. The carbon peaks are not observed possibly due to the poor crystallinity. The TEM images of the SnSe/NC nanobelts in Fig. 2B and C display that the thickness of the nanobelts is about 5–8 nm (as seen in the histogram in Fig. 2C). The SnSe nanofilaments are perpendicular to the axial direction of the nanofilaments consistent with the SEM image. The representative HR-TEM image (Fig. 2D) shows the multilayered structure of SnSe with a layer spacing of 0.58 nm corresponding to (200) plane, further confirming the vertical growth of SnSe nanofilaments. The high-angle annular dark-field scanning TEM (HAADF-STEM) image and corresponding element maps (Fig. 2E) of SnSe/NC confirm the uniform distribution of Sn, Se, C, and N. The atomic ratio of Sn in SnSe/NC is calculated to be 12.3:11.9 based on EDS, which is close to the stoichiometric ratio of SnSe (Fig. S5). The thermogravimetric results (TGA) obtained from SnSe/NC reveal that the carbon content in SnSe/NC is about 8.8 wt% (Fig. S6). The nitrogen adsorption results of SnSe/NC are shown in Fig. S7 and the Brunauer-Emmett-Teller (BET) surface area is measured to be 39 m² g⁻¹.

X-ray photoelectron spectroscopy (XPS) is conducted to determine the composition and chemical states. The survey spectrum of SnSe/NC (Fig. S8) shows the presence of Sn, Se, C, and N. The high-resolution Sn 3d spectrum in Fig. 2A shows two peaks at 486.0 eV and 494.3 eV attributed to Sn 3d5/2 and Sn 3d3/2 of Sn²⁺ in SnSe/NC [19]. The Se spectrum reveals two peaks at 527.2 and 536.6 eV corresponding to Se 3d5/2 and Se 3d3/2 of Se²⁻ in the SnSe/NC nanobelts (Fig. 3B) [20]. For comparison, pure SnSe nanofilaments are also prepared by the direct cation-exchange reaction of ZnSe(DETA)0.5 in the SnSO₄ solution. During the cation-exchange process, the interlayered DETA molecules in ZnSe(DETA)0.5 dissolve in water and thus the SnSe nanofilaments are produced, which are confirmed by SEM (Fig. S9A and B) and XRD (Fig. S9C). Compared to the pure SnSe, the Sn and Se peaks in the SnSe/NC nanofilaments shift to higher binding energy and the formation of Sn-C bonding is identified in high-resolution Sn3d and Cls spectra (Fig. 3C) [21,22], suggesting the formation of electronic charge coupling between the SnSe and NC. The N1s spectrum can be deconvoluted into three peaks corresponding to pyridinic, pyrrolic, and graphitic nitrogen, respectively, which supports the existence of N heteroatoms (Fig. 3D). The Raman spectra of SnSe/NC and SnSe (Fig. 3E) exhibit two broad peaks at 1347 and 1574 cm⁻¹ for SnSe/NC related to the D and G bands of NC, respectively [23]. The N doping in NC result in the broadening and overlapping of D and G bands, and an asymmetric tailing of the D band extending out to about 1000 cm⁻¹ [24]. The Raman peaks at 1311.1 cm⁻¹ (A₁g) and 1605.5 cm⁻¹ (A₂g) are the rigid shear modes of the SnSe layer against its neighbours along the a/b-axes [25]. Compared to SnSe, the Raman peaks of SnSe/NC shift to high frequencies due to the reinforced steric hindrance caused by the strong electron interaction between SnSe and NC [26].

The aforementioned results demonstrate that the vertical SnSe nanofilaments on NC with Sn-C bonding are produced via the cation-exchange process. The SnSe has an orthorhombic layered crystal structure with atoms arranged in two adjacent double layers of Sn and Se forming a planar bilayer structure. Strong covalent bonds are present in the atomic layers (b/c-axes) but the interlayer van der Waals force (a-axis) is weak. The anisotropic atomic bonding nature of SnSe causes faster growth along the b/c-axes than the a-axis, which is favourable to the formation of SnSe nanofilaments [27]. The Sn-Se-Sn bond in the ⟨h00⟩ plane has a zigzag shape and the Sn atoms at the end-face are bare. The barely terminated Sn atoms are more likely to form Sn-C bonding with C in the NC layers during the cation-exchange process. Hence, SnSe grows vertically and preferentially on the NC due to the influence of Sn-C bonding, resulting in vertical SnSe nanofilaments (Fig. 3F). Compared to SnSe/NC, the pure SnSe fabricated using the similar cation exchange with ZnSe(DETA)0.5 as precursors consists of the aggregated tined nanofilaments (Fig. S9A and B), confirming the importance of NC to the growth of vertical SnSe nanofilaments.

To theoretically elucidate the interfacial Sn-C bonding in SnSe/NC, DFT calculations are conducted. We considered four kinds of model with different SnSe surfaces and carbon types in order to judge the stability of carbon-SnSe interface structures (Fig. S10). There are Sn-terminated atom with C (Sn/C), Se-terminated atom with C (Se/C), terminated Sn atom with NC (Sn/NC) and terminated Se atom with NC (Se/NC). The low single bond energy are about −0.1 eV for Sn/C and Se/C structure models, indicating the weak van der Waals interaction between SnSe and carbon. In the Sn/NC model, the terminated Sn atom adheres to the C atoms of NC, accompanying with large distortion of carbon surface. Fig. 3G displays the geometrically optimized model of SnSe/NC with Sn-C chemical bonding. The average Sn-C bonding distance is 2.44 Å, which is very close to the Sn-C length in SnC crystal (2.20 Å). Meanwhile, the single Sn-C bond energy is as large as 1.25 eV, indicating the strong chemical bond between SnSe and NC (Fig. S10C). The charge distribution of SnSe/NC is also revealed by the charge density differences as shown in Fig. 3H. Compared to that of the SnSe/C model without presence of Sn-C bonding (Fig. S11), there is more significant charge redistribution at the Sn-C interface region in SnSe/NC. The accumulated charge at the interface of SnSe/NC confirms the enhanced charge transfer between NC and SnSe through Sn-C bonding, which is expected to greatly improve the rate performance and structural stability of the electrode during discharge/charge process.

The Na-ion storage performance is evaluated by galvanostatic charging-discharging (GCD), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The test of the cycling stability of the SnSe/NC and SnSe nanofilaments is described in Fig. 4A and Fig. S12. The SnSe/NC nanofilaments exhibit large capacities of 723 mA h g⁻¹ at 25 mA g⁻¹ after 50 cycles, which are larger than most previously reported anode materials for SIBs (See Table S1). The SnSe/NC nanofilaments display excellent cycling stability as manifested by 82% capacity retention (258 mA h g⁻¹) for over 200 cycles at 2 A g⁻¹, but on the other hand, the capacity of pure SnSe decays to almost zero after 200 cycles. The SnSe/NC nanofilaments have a high coulombic efficiency (CE, nearly 100%) after 5 cycles and the initial irreversible capacity (initial CE of about 77%) is due to the formation of solid electrolyte interphase films (SEI). The structural stability of SnSe/NC is confirmed from the SEM images after 200 cycles at 2 A g⁻¹ (Fig. S13). The nanofilaments morphology of SnSe/NC is well retained after cycling, while the morphology of pure SnSe becomes aggregation, indicating that the presence of NC in SnSe/NC can effectively limit the aggregation of SnSe during the sodiation/desodiation processes. The SnSe/NC nanofilaments also have higher rate capability than SnSe nanofilaments (Fig. 4B). The specific capacities of the SnSe/NC nanofilaments are 570, 527, 445, 385, 304, 218 and 100 mA h g⁻¹ at current densities of 0.1, 0.2, 0.5, 1, 2, 5 and 10 A g⁻¹, respectively. Even at 20 A g⁻¹, the SnSe/NC nanofilaments still show a high capacity of 88 mA h g⁻¹. Moreover, the SnSe/NC also exhibits high volumetric capacities of 415, 400, 342, 292, 232, 160, 107 and 65 mA h cm⁻³ at current densities of 0.1, 0.2, 0.5, 1, 2, 5, 10 and 20 A g⁻¹, respectively, as shown in Fig. S14. The EIS results after the 5th desodiation state are presented in Fig. 4C. The semicircle in high- and medium-frequency zone can be usually related to the charge transfer impedance (Rct) of the electrode, while the line in low-frequency region is associated with the Warburg resistance reflecting the
The intercept in real axis is related to the ohmic resistance ($\text{Rs}$), including the inherent resistance of electrode materials, the contact resistance and the ionic and electronic resistances. For SnSe/NC, the $\text{Rs}$ ($9.6\ \Omega$) is slightly smaller compared to SnSe electrode ($10.3\ \Omega$) due to the enhanced conductivity of NC. Moreover, the SnSe/NC electrode delivers the smaller charge transfer impedance than that of pure SnSe, demonstrating the smaller interface resistance and enhanced charge transfer kinetics [28].

The charge storage behavior and reaction kinetics of the SnSe nanobelts are further analysed by correlating the currents ($i$) with scanning rates ($v$) based on Equation: $i = a v^b$, where $b$ reflects the charge storage behavior [29]. In the diffusion-controlled process (battery behavior), $b$ is equal to 1.0, whereas in the surface-controlled (capacitor behavior) process, $b$ is 0.5. Fig. 4D shows the CV curves of the SnSe/NC electrode at scanning rates between 0.1 and 5 mV s$^{-1}$ and a well-preserved shape is observed with increasing sweeping rates. The $b$ values of the anodic and cathodic peaks are 0.80 and 0.81 of the SnSe/NC nanobelts (Fig. 4E), implying that Na-ion storage is controlled mainly by surface pseudocapacitive reactions. The $b$ values of the anodic and cathodic peaks of the pure SnSe electrode are calculated to be 0.59 and 0.55, respectively (Fig. S15B and C) indicative of diffusion-controlled Na-ion storage processes. The quantitative storage contributions in SnSe/NC can be evaluated by separating the current response ($i$) at a fixed voltage based on Equation: $i(V) = k_1 v + k_2 v^{1/2}$, where $k_1$ and $k_2$ are constants obtained from the linear plots of $i(V)/v^{1/2}$ vs $v^{1/2}$ at a certain voltage and the pseudocapacitance and diffusion-controlled capacity can be quantitative calculated by separating the current response $i$ into $k_1 v$ and $k_2 v^{1/2}$ [30]. Fig. 4F reveals that the pseudocapacitive contribution ratios of SnSe/NC increases from 57.9% to 84.2% for 0.3–5 mV s$^{-1}$. The big proportion of pseudocapacitive contribution enables enhanced rate performance of SnSe/NC. To elucidate the dynamic resistance variation and overpotential difference between the SnSe/NC and SnSe electrodes, galvanostatic intermittent charging and discharging are performed to obtain the direct current internal resistance (DCIR) [31]. The SnSe/NC has lower reaction resistance and interfacial resistance during charging and discharging (Fig. S16), resulting in improved surface redox kinetics compared to the SnSe nanobelts.

The density of states (DOS) are calculated to further elaborate the electronic conductivity of structure. It can be observed that the calculated pure SnSe has a band gap (about 0.61 eV), showing a semiconductor behavior (Fig. 4G). In contrast, there is no band gap around the Fermi level for SnSe/NC, indicating its conductor characteristic.

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**Fig. 3.** High-resolution XPS spectra of (A) Sn 3d, (B) Se 3d, and (C) C 1s in SnSe/NC and SnSe. (D) High-resolution XPS spectra of N1s in SnSe/NC. (E) Raman scattering spectra of SnSe/NC and SnSe. (F) Schematic Illustration of the vertical SnSe nanoplates on NC. (G) Geometrically optimized model of SnSe/NC structure with strong Sn-C bonding. (H) Charge density difference for SnSe/NC model, the yellow and blue cloud represent the negative and positive charge differences, respectively (isosurface value is $\pm 0.001\ \varepsilon$ per $\text{Å}^3$).
The partial DOS shows that this conductor characteristic is mainly attributed to the change of Fermi level (decline of SnSe and rise of NC) caused by the charge redistribution along Sn-C bonding. Thus, the electrons can easily flow along the NC and fast transfer to SnSe through the Sn-C bonding. We then figure out the Na\(^+\) diffusion energy barriers along the different pathway to explore the ionic conduction in SnSe interlayer. The results are illustrated in Fig. 4I. Astonishingly, the calculated Na\(^+\) diffusion barrier is 0.27 eV along z axis and as low as 0.1 eV along y axis in the interlayer of SnSe, which is lower than the reported values in 1T-MoS\(_2\) (0.28 eV)\(^{10}\), SnO\(_2\) (0.41 eV)\(^{11}\), Sb\(_2\)S\(_3\) (0.19) \(^{12}\), and black P (0.18 eV)\(^{13}\), even lower than Li\(^+\) diffusion barrier in bilayer MoS\(_2\) (0.32 eV)\(^{32}\), Li\(_3\)VO\(_4\) (0.49 eV)\(^{33}\), ReS\(_2\) (0.39 eV)\(^{34}\), and graphite (0.5 eV)\(^{35}\). Such a low diffusion barrier is related to the intrinsic channel along y axis and non-rigid structure of SnSe, which will occur the flexible bending or distortion of Sn-Se bond to adapt the Na\(^+\) diffusion (Fig. S17). The riveted structure of vertical SnSe nanoplates on NC and the low diffusion barrier of SnSe favour the enhanced electrochemical kinetics of SnSe/NC for Na-ion storage.

To understand the electrochemical reactions and phase variation of SnSe in SIBs, CV, ex-situ Raman and ex-situ XRD techniques are investigated. Fig. 5A shows the CV curves of SnSe/NC from the 1st to 5th cycles. The SnSe electrode displayed the similar redox peaks with SnSe/NC electrode in the 0.1 mV s\(^{-1}\) as shown in Fig. S15A. The broad weak cathodic peak at 1.2 V in the 1st discharge process is ascribed to the intercalation of Na\(^+\) into the interlayer of SnSe. The wide peak at 0.82 V is attributed to the reduction of SnSe to Sn and formation of Na\(_x\)Sn as well as solid electrolyte interphase (SEI) layers. The sloping line below 0.5 V arises from the gradual alloying reaction between Sn and Na ions forming Na\(_x\)Sn. The anodic peaks at 0–0.9 V during the charging process stem from the stepwise desodiation reaction from Na\(_x\)Sn to Na-Sn intermediates and final Sn \(^{36}\). The anodic peak at 1.21 V is due to the conversion of Sn to Na\(_x\)Sn and the weak peak at 1.58 V may stem from the deintercalation of Na\(^+\) from the interlayer of SnSe. In the ongoing cycle, the CV curves of SnSe/NC overlap well and high reversibility is indicated. The structural and compositional evolution of SnSe/NC electrode during the sodiation/desodiation process are investigated by the ex-situ XRD (Fig. 5B and C) and ex-situ Raman scattering techniques (Fig. S18). When the cell discharges to 1.2 V, the XRD peaks of SnSe/NC slight shift to lower degree, which is possibly due to the sodium intercalation reaction and formation of intermediate (SnSe + xNa\(^+\) → Na\(_x\)SnSe). With further discharging, the XRD peaks of Sn appear at 0.6 V and gradually decrease until disappear at 0.001 V, indicating the decomposition of Na\(_x\)SnSe to Sn and then convert into amorphous Na\(_x\)Sn alloy (Na\(_x\)Sn + xNa\(^+\) → Sn + Na\(_x\)Sn, Sn + xNa\(^+\) → Na\(_x\)Sn). The Na\(_x\)Sn can be detected by the Raman shift (249 cm\(^{-1}\)) in the fully discharging state (Fig. S18)\(^{37}\), while no peak is assigned to Na\(_x\)Sn in XRD pattern, confirming its amorphous characteristic. Upon recharging, the intensities of Sn peaks undergo strengthened and then weakened before 1.5 V following by the reappearance of Na\(_x\)SnSe. When the cell is fully charged, SnSe is

![Fig. 4. (A) Cycling performance and coulombic efficiency. (B) Rate capability of the SnSe/NC and pure SnSe electrodes. (C) Nyquist plots of the SnSe/NC and SnSe electrodes. The inset displays the equivalent circuit and high frequency regain profile. (D) CV curves of SnSe/NC at various scan rates. (E) The corresponding relationship between log (sweep rate) and log (peak current) of SnSe/NC. (F) Capacity contribution ratios of SnSe/NC for different scanning rates. Calculated DOSs of (G) SnSe and (H) SnSe/NC. (I) Na\(^+\) diffusion pathway and corresponding energy profile in the interlayer of SnSe.](image-url)
reformation, which can be also demonstrated from the Raman scattering (Fig. S18).

We also use DFT to further explore the reversibility of SnSe/NC for Na⁺ storage. As shown in Fig. 5D and Fig. S19, the structure of SnSe/NC remains almost unchanged when one Na⁺ intercalates into the interlayer of SnSe. With the amount of intercalated Na⁺ increasing (Na:Se = 1:1), the structure become some distorted, whereas the structure can be returned to original by optimizing the structure with subtracting the Na⁺. When the amount of intercalated Na⁺ are twice of Se atoms, the structure possesses further distortion, along with the separation of Sn atoms and formation of Sn-Sn bonding, which is consistent with the ex-situ XRD results. Although the original structure of SnSe/NC is thermodynamically more stable, the transform from Sn/NC to SnSe/NC need a barrier of 0.14 eV per SnSe unit cell (Fig. 5E and Fig. S20). The low recovered barrier suggests the fast electrochemical kinetics and excellent reversibility of SnSe/NC for Na⁺ storage. The HR-TEM images can confirm the recovery of SnSe/NC at the full charging state after 5 cycles (Fig. 5F and G), further confirming the good stability and reversibility of the SnSe/NC during sodiation/desodiation process. The increased interlayer distance of the SnSe nanoplates (0.92 nm) in Fig. 5G from pristine 0.58 nm (Fig. 2D) is attributed to the repeated insertion/extraction of Na⁺ [22,38].

The superior Na-ion storage performance of SnSe/NC is attributed to the unique structure as schematically depicted in Fig. 6. Firstly, the SnSe/NC with Sn-C bonding exhibits an improved electrical conductivity. The electrons can easily flow along the NC and fast transfer to SnSe through the Sn-C bonding, leading to lower interface contact resistance and smaller polarization, especially at high current densities. Secondly, the small and thin SnSe nanoplates with layered and open structure, as well as the extremely low Na⁺ diffusion barrier (0.1 eV), can provide the fast interlayer Na⁺ diffusion channel, enabling enhanced rate performance and pseudocapacitive charge storage. Thirdly, the riveted structure of SnSe on NC via Sn-C bonding could effectively prevent the aggregation of SnSe during cycling. Meanwhile, the low energy barrier from discharged-SnSe/NC to pristine SnSe/NC demonstrates the easy recoverability of SnSe/NC from the discharged product, suggesting superior cycling performance. All in all, this hybrid structure shows high utilization of the active materials, good electrode integrity, fast electrode reaction kinetics, superior cycling stability, as well as high energy and power densities.

4. Conclusion

In summary, vertical SnSe on NC hybrid nanobelts with Sn-C bonding are synthesized by a facile cation-exchange method. The SnSe/NC delivers superior performance as anode materials in SIBs such as a
Fig. 6. Schematic illustration of high rate performance of SnSe/NC.

high reversible capacity of 723 mA h g\(^{-1}\) at 25 mA g\(^{-1}\). Boasting the thin nanoplates and riveted structure of SnSe on NC, SnSe/NC exhibits a high rate capability of 88 mA h g\(^{-1}\) at 20 A g\(^{-1}\) and good cycling performance with 82% capacity retention for over 200 cycles at 2 A g\(^{-1}\). DFT calculations demonstrate that the presence of N heteroatom in NC matrix promote the formation of Sn-C bonding. The SnSe has an extremely low interlayer Na\(^+\) diffusion barrier (0.1 eV), and exhibits small energy barrier (0.14 eV/uc) from discharged product (Sn) to pristine SnSe/NC, indicating the fast electrochemical kinetics and good reversibility of SnSe/NC. Our results offer insight into the design of high-performance hierarchical metal sulfides and selenides with chemical bonding in advanced SIBs.

Acknowledgements

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2018.10.019

References

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Supplementary Information

Sn-C Bonding Riveted SnSe Nanoplates Vertically Grown on Nitrogen-Doped Carbon Nanobelts for High-Performance Sodium-Ion Battery Anodes

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**Fig. S1.** (A) SEM image and (B) TEM image of the ZnSe(DETA)$_{0.5}$ nanobelts.

**Fig. S2.** XRD patterns of ZnSe(DETA)$_{0.5}$ and ZnSe/NC.
Fig. S3. (A) SEM image, (B) TEM image, (C) HR-TEM image and (D) elemental maps of ZnSe/NC.

Fig. S4. Raman scattering spectra of ZnSe/NC.

The two peaks at 1355 and 1580 cm$^{-1}$ are ascribed to the D band and G band of the N-doped carbon. The G-band is related to the sp$^2$ carbon atoms vibration in a 2D hexagonal lattice, and the D-band is attributed to the presence of defects and disorders in the carbon lattice. [1] The N doping in carbon could cause the broadening and overlapping of D and G bands, and also lead to an asymmetric tailing of the D band extending out to about 1000 cm$^{-1}$. [2]
Fig. S5. EDS spectrum and elemental content of SnSe/NC.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>42.20</td>
<td>12.3</td>
</tr>
<tr>
<td>Se</td>
<td>27.16</td>
<td>11.9</td>
</tr>
<tr>
<td>C</td>
<td>10.51</td>
<td>30.3</td>
</tr>
<tr>
<td>N</td>
<td>3.35</td>
<td>8.4</td>
</tr>
</tbody>
</table>

Fig. S6. TGA curves of SnSe/NC and SnSe.

The TGA curves of SnSe first show a weight gain from room temperature to 400 °C due to partial oxidation of SnSe to SnSeO$_x$.\textsuperscript{1} The next weight loss is related to the loss of formed volatile SeO$_2$ when SnSeO$_x$ is oxidized to SnO$_2$ as the temperature goes up. In comparison, SnSe/NC shows a greater mass loss on account of the extra loss of nitrogen-doped carbon.
Fig. S7. Nitrogen adsorption/desorption isotherms and pore size distributions (inset) of SnSe/NC.

Fig. S8. Survey XPS spectra of SnSe/NC.
Fig. S9. (A, B) SEM images and (C) XRD pattern of pure SnSe.
Fig. S10. Geometrically optimized model of SnSe with C heterostructure with van der Waals correction. (A) Terminated Sn atom with C, (B) terminated Se atom with C, (C) terminated Sn atom with NC and (D) terminated Se atom with NC. (E) The single energy ($E_{\text{single}}$) and bonding distance for the different optimized model.

DFT calculations are performed to judge the stability of carbon-SnSe interface structures. We set four kinds of model with different SnSe surfaces and carbon types. There are Sn-terminated atom with C (Sn/C), Se-terminated atom with C (Se/C), terminated Sn atom with NC (Sn/NC) and terminated Se atom with NC (Se/NC). In the Sn/C and Se/C structure models, the average distance between the SnSe and C is 3.51 and 3.56 Å, respectively, and the carbon surface remains flat, suggesting the negligible interaction between SnSe and carbon. Then, we study the binding energy by $E_b = E_{\text{total}} - E_{\text{carbon}} - E_{\text{SnSe}}$, where $E_{\text{total}}$, $E_{\text{carbon}}$ and $E_{\text{SnSe}}$ are the total energy of the hybrid structure, carbon and SnSe, respectively. The single energy
can be given by $E_{\text{single}} = \frac{E_b}{n}$, where $n$ is the number of Sn-C (Se-C) bondings. The low single energy are about -0.1 eV for Sn/C and Se/C structure models, indicating the weak van der Waals interaction between SnSe and carbon. Follow the influence of N doping on the stability was investigated. In the Sn/NC model, the terminated Sn atom adhere to the C atoms, accompanying with the distortion of carbon surface. The average Sn-C distance is 2.44 Å, which is very close to the length of Sn-C in SnC crystal (2.20 Å) and much shorter than the distance in Se/NC model (2.77 Å). Meanwhile, the single Sn-C bond energy is as large as 1.25 eV, indicating the good stability of Sn-C bonding between NC and SnSe surface.

Fig. S11. Charge density difference for SnSe/C model without the presence of Sn-C bonding (isosurface value is $\pm0.00035$ $e$ per Å$^3$).

Fig. S12. Cycling stability of SnSe/NC at a current density of 25 mA g$^{-1}$.
**Fig. S13.** SEM images of (A) SnSe/NC and (B) pure SnSe electrodes after 200 cycles at 2 A g\(^{-1}\).

**Fig. S14.** (A) Cross-section SEM image of the SnSe/NC electrode, (B) volumetric capacities of the SnSe/NC electrode at various current density. The volumetric capacity of the SnSe/NC can be calculated through the equation:

\[
C_v = C_m \cdot \rho = \frac{C_m \cdot m}{S \cdot d}
\]

Where \(C_v\) is the volumetric capacity; \(C_m\) is the mass specific capacity; \(\rho\) is the packing density of the electrode material; \(m\) is the mass of the electrode material (0.57 mg); \(S\) is the electrode area (0.2827 cm\(^2\), diameter is 0.6 cm) and \(d\) is the thickness of the electrode. The thickness of the electrode is measured to be 26.2 μm.
**Fig. S15.** (A) CV curves of SnSe electrode at 0.1 mV s\(^{-1}\). (B) CV curves of SnSe electrode at various scan rates. (C) The relationship between log (sweep rate) and log (peak current) of SnSe.

**Fig. S16.** DCIR test profiles of (A) SnSe/NC and (B) SnSe based on the galvanostatic intermittent charging and discharging method; Direct current internal resistance of SnSe/NC and SnSe electrodes in the (C) discharging and (D) charging processes.

The DCIR method introduces a periodical current pulse input and following relaxation stage during the sodiation/desodiation process. The DCIR is derived from Ohm's law and the lumped resistance can be calculated by the ratio between the voltage change at the relaxation
stage (60 s) and pulse current during discharging and charging. This technique shows the significance to evaluate the electrochemical performance among different materials.

**Fig. S17.** Optimal Na diffusion pathway along z (A) and y (B) axes in the interlayer of SnSe.

**Fig. S18.** *Ex-situ* Raman spectra of SnSe/NC at different discharge/charge states.
Fig. S19. (A) The structure of SnSe/NC after different amount of Na\(^+\) intercalation and (B) the corresponding optimized structure with subtraction of Na\(^+\). (I) One Na\(^+\) intercalation. (II) and (III) The ratio between intercalated Na\(^+\) and Se atom is 1:1 and 2:1, respectively.

Fig. S20. The recovered pathway from the discharged-SnSe/NC to pristine SnSe/NC structure. The pathway are optimized with the nudged elastic band method.
Table S1. Comparison of the results in our study with those previously reported for Na-ion batteries.

<table>
<thead>
<tr>
<th>Type of materials</th>
<th>Capacity (mA h g(^{-1}))</th>
<th>Current density (mA g(^{-1}))</th>
<th>Cycle number (cycles)</th>
<th>Reference</th>
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<td>SnSe nanoplates</td>
<td>558</td>
<td>300</td>
<td>50</td>
<td>3</td>
</tr>
<tr>
<td>SnSe/C composite</td>
<td>707</td>
<td>143</td>
<td>50</td>
<td>4</td>
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<td>SnSe nanosheet clusters</td>
<td>183</td>
<td>2000</td>
<td>100</td>
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<td>2D SnSe Nanoplates</td>
<td>393</td>
<td>50</td>
<td>300</td>
<td>6</td>
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<td>SnTe/amorphous C</td>
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<td>50</td>
<td>100</td>
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<td>Hollow Sb@C yolk-shell Spheres</td>
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<td>Amorphous SnO(_2)</td>
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<td><strong>SnSe/NC nanobelts</strong></td>
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