Electronic Supplementary Information (ESI)

High yield electrochemical exfoliation of tin selenide quantum dots

for high-performance lithium-ion batteries[†]

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1. Supplementary methods.

Electrochemical Exfoliation of Bulk SnSe: The electrochemical exfoliation of bulk SnSe was performed using an electrochemical workstation (CHI 760E) in a twoelectrode system. Bulk SnSe (Fig. S1⁺) was fixed in a Pt clamp as the working cathode and a Pt wire was used as the counter electrode. A solution consisting tetra-butyl ammonium tetrafluroborate and propylene carbonate (PC) solvent was used as electrolyte. All the solvents and ammonium ions compound were purchased from Sigma Aldrich (>99% of purity) and used as received. The exfoliation of SnSe QDs was carried out under a cathodic potential ranging from -5 to -7.5 V. The exfoliated SnSe solution was further treated by bath sonication (at 100 W for 10 min) to obtain the well-dispersed SnSe QDs.

Electrochemical Measurement: To investigate the lithium-storage performance, we prepared a uniform slurry by stirring SnSe QDs (75 wt%) mixed with Super P carbon black (10 wt%) and sodium alginate (15 wt%) in isopropyl alcohol for more than 12 hours. We then coated the slurry onto the 25 μ m copper foil, which was further dried at 80 °C in vacuum oven for 24 h. Subsequently, it was cut into discs with a diameter of 12 mm for coin cell assembly. The CR2016 coin cells were assembled in an Ar-filled glovebox using lithium metal as reference and counter electrode, and a glass microfiber filter (Whatman) as the separator. 1 M LiPF₆ in anhydrous PC was used as the electrolyte. The cell was galvanostatically discharged/charged at various current densities in the voltage range of 0.005-3.0 V (versus Li/Li⁺) using a Bitrode battery tester system (Model SCN-12-4-5/18) with a data collection time interval of 0.3 s.

Characterization: STEM-ADF imaging was carried out using an aberration-corrected JEOL ARM-200F, equipped with a cold field emission gun, operating at 60 kV. STM imaging was performed at 4.5 K in Omicron LT-STM system using a chemically etched tungsten tip. The morphology of bulk SnSe and exfoliated SnSe QDs was

characterized by SEM (FEI Verios 460 operated at 2 kV and 100 pA), AFM (Bruker Multimode 8) and HRTEM (FEI Titan 80-300 S/TEM operated at 200 kV). Raman spectroscopy measurement of exfoliated BP (WITec Alpha 300R) was performed at room temperature with the laser excitation at 532 nm. XPS (SPECS XR-50) elemental analysis of exfoliated BP was conducted using Al K α radiation (hv=1486.6 eV).

2. Bulk SnSe.

Growth of bulk SnSe:

High quality SnSe single crystals are synthesized by a modified Bridgeman method¹, which yields centimetre-sized crystals. Sn powder (99.999% Alfa Aesar) and Se powder (99.999% Alfa Aesar) were mixed stoichiometrically before loading into a quartz tube in a glove box filled with argon. The quartz tube was evacuated to a pressure of 10⁻² Pa, and was flame-sealed immediately. The quartz tube was then put into a tube furnace. For crystal growth, the furnace temperature was increased slowly from room temperature to 1223 K, which was held for 25 hours to ensure a uniform flux. The temperature setpoint was then ramped to 973K for 72 hours to prevent the local phase segregation of SnSe₂ microdomains. After that, the furnace temperature was directly set to room temperature, which allow the samples to be naturally cooled down within 10 hours.



Fig. S1 Photograph and Raman spectrum of single crystal SnSe.

3. Electrochemical exfoliation of bulk SnSe.

In order to prevent anodic oxidation, we carried out the cathodic exfoliation of bulk SnSe using ammonium cations as the intercalant. In addition, the size of ammonium cation in electrolyte can be tuned by changing the length of alkyl chain and its surrounding solvent molecules.² It is found that TBA cations dissolved in PC serve as effective intercalants for the intercalation and exfoliation of the bulk SnSe. Fig. S2 shows the electrochemical exfoliation of bulk SnSe at -5 V in 0.05 M TBA/PC electrolyte. Under this condition, we observe a coexistence of SnSe QDs (Fig. S2b) and nano-flake structures (Fig. S2c-d). As-exfoliated SnSe nano-flakes show an average size of ~20 nm (Fig. S2c). In addition, our HR-TEM imaging also captured the orthorhombic lattice fringes of exfoliated SnSe nanostructures (Fig. S2d).^{3, 4} AFM image and the corresponding height profile reveals that the averaged thickness of these nano-flakes is below 10 nm as shown in Fig. S2e-f. We also note that the cathodic exfoliation of bulk SnSe into nanostructures can be achieved using TBA dissolved in several aprotic polar solvents including N-methyl pyrrolidone, N,Ndimethylformamide and dimethyl sulfoxide.



Fig. S2 Morphology characterization of exfoliated SnSe QDs under a cathodic potential of -5 V in 0.05 M TBA/PC electrolyte. (a) Large-scale and (b-c) Zoom-in TEM image of exfoliated SnSe. (d) HR-TEM image of exfoliated SnSe nano-flakes with the corresponding FFT pattern (inset). (e) AFM image of exfoliated SnSe nanostructure with the corresponding (f) height profiles as marked by dashed circle in panel (e).

4. Cathodic potential dependent current curve for bulk SnSe in TBAB/PC.



Fig. S3 Electrochemical current as a function of cathodic potential applied in the PC electrolyte containing 0.2 M TBAB. The broad peak at \sim -2.5 V vs Pt can be ascribed to the intercalation of ammonium ions into the interlayer of SnSe.

5. The discussion of intercalation mechanism.





The initial bulk SnSe reveals a layer-stacked structure as shown in Fig. S4a After applying a cathodic potential of -5 V for 5 min, the edge of SnSe crystal becomes rough with the formation of tiny holes as shown in Fig. S4b. A high cathodic potential of -7.5 V increases the intercalation rate significantly which results in a much higher density of holes at the edge of bulk SnSe. A zoom-in SEM image (Fig. S4c) of the edge of bulk SnSe after applying the exfoliation voltage of -7.5 V for 5 mins.

As illustrated in Fig 1a, the electrochemical intercalation and decomposition of intercalants in the interlayer galleries of bulk materials can result in expansion force along both interlayer and intralayer directions. Strong intralayer bonding strength

favors the intercalation of a large amount of intercalants for a long period of time, leading to a large intercalation depth. A strong interlayer bonding strength results in a high intercalation barrier, leading to a slow intercalation rate and small intercalation depth. As for SnSe, the weak intralayer Sn-Se bonding can be readily broken upon the application of a strong intercalation force, resulting in the exfoliation of bulk SnSe into small flakes. Moreover, a relatively strong interlayer vdW bonding strength in SnSe (~1.5 times stronger than that of BP) also limits the intercalation depth. This also favors the synthesis of small-sized SnSe QDs. 6. STEM-ADF image of exfoliated SnSe QDs.



Fig. S5 (a) Large-area STEM-ADF image of SnSe QDs exfoliated by applying a cathodic voltage of -7.5 V vs Pt. (b) A close-up STEM image of as-exfoliated SnSe QDs.

7. Uv-vis absorption spectrum of SnSe QDs in PC.



Fig. S6 Uv-vis absorption spectrum of SnSe QDs dispersed in PC.

8. LIBs performance of large-sized SnSe anode materials.

To probe the size effect, large-sized SnSe nanoparticles (NPs) (tens of nanometer) were exfoliated at -5 V in 0.02 M TBA/PC electrolyte. The large-sized SnSe NPs are used as anode materials in LIBs (Fig. S7). In contrast to SnSe QDs, the peak at ~ 1.85 V associated with the reversible formation of SnSe is absent for SnSe NPs during electrochemical charging/discharging. This suggests an irreversible conversion of large-sized SnSe NPs in LIBs.

Fig. S7d shows the cycle performance of SnSe NPs at a current density of 0.5 A g⁻¹. An initial capacity of ~ 827 mAh g⁻¹ can be achieved using pristine SnSe as anode. However, it decays rapidly to 190 mAh g⁻¹ after 80 cycles, consistent with the previous results for bulk SnSe anode materials⁵⁻⁸. The fast decay of capacity can be reflected in the rate performance as revealed in Fig. S7e. The initial capacity of SnSe is determined to be ~ 1027 mAh g⁻¹ at a current density of 0.1 A g⁻¹, while the capacity decreases rapidly to 504 mAh g⁻¹ after 30 cycles of charging/discharging test at various current densities.



Fig. S7 Electrochemical performance of large-sized SnSe nanoparticles (~40 nm) used in half-cells for lithium storage. (a) Large-scale and (bottom inset) Zoom-in TEM images of as-exfoliated SnSe with the averaged size of tens of nanometers. (b) Statistical analysis of the size distribution of SnSe NPs based on TEM measurement. (c) CV curves for the initial cycles of SnSe nanoparticles at a scanning rate of 0.1 mV/s. (d) Cycle performance (a current density of 0.5 A g⁻¹) and (e) rate capability of SnSe NPs with an average size of ~40 nm

The following equations can be used to describe the electrochemical reactions of tin-

based IV-VI materials at the anode of LIBs^{8, 9}:

Initial discharge process:

 $SnSe_x + 2Li^+ + 2e^- \longrightarrow Sn + xLi_2Se$ (1)

 $Sn + 4.4Li^+ + 4.4e^- \longrightarrow Li_{4.4}Sn$ (2)

Subsequent cycles:

 $Li_{4.4}Sn \longrightarrow Sn + 4.4Li^+ + 4.4e^-$ (3)

Generally, the formation of Li_2Se is considered as a partially reversible or fully irreversible process in the LIBs. The reversible alloying process (equation (2) and (3) between Sn and Li can deliver a theoretical capacity of 596 mAh g⁻¹. In this work, a reversible capacity of 830 mAh g⁻¹ can be obtained using SnSe QDs as anode materials. This indicates an extra capacity contribution from the reversible conversion of Li_2Se as described by the following equation:

Li₂Se conversion:

 $Li_2Se + Sn \longrightarrow SnSe + 2Li^+ + 2e^-$ (4)

9. Structure analysis of post-cycled SnSe QDs

The morphologies of anode materials after 200 charge-discharge cycles at a current density of 0.5 A g⁻¹ were studied using HRTEM. As revealed in the large-area (Fig. S8a) SEM and (Fig. S8b) TEM images, SnSe QDs with the averaged size of 3-5 nm are uniformly dispersed on carbon black after performing multiple cycles of charging/discharging. In addition, the observation of orthorhombic atomic lattice¹⁰ (Fig. S8c) of SnSe QDs further proves that SnSe QDs can be regenerated in the delithiation process.



Fig. S8 (a) SEM and (b-c) HRTEM images of the SnSe QDs anode after 200 cycles of

test under a discharge/charge current density of 0.5 A g⁻¹.

	Rs (Ω)	Rct (Ω)	Zw (Ω)
1 st	4.4	249.2	52.7
2 nd	4.3	162.4	38.9
1000 th	4.1	107.7	22.4
1500 th	4.1	103.5	20.9

10. A summary of resistances simulated with equivalent electric circuit in Fig. 4e.

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