Supporting Information

Yolk-shell structured SnSe as a high-performance anode for

Na-ion batteries

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Experimental Section

Chemicals: Tin (II) chloride (SnCl₂, 99%) and hexacarbonyl tungsten (W(CO)₆, 97%) were purchased from Alfa Aesar. Hexamethyldisilazane (HMDS, 99%), oleylamine (OAm, 70%), 1-octadecene (ODE, 90%), trin-octylphosphine (TOP, 97%), and Se pellets (99.99%) were purchased from Aldrich. OAm and ODE were dried under vacuum at 120 °C for 1 h and then stored under an Ar atmosphere prior to use. All other reagents were used as received.

Synthesis of SnSe nanoparticles: Monodisperse SnSe nanoparticles were synthesized in large quantity by a modified method based on our previous recipe.¹ Before the reaction, TOP-Se solution (1 mmol/mL) was prepared in the glovebox by stirring the certain amounts of TOP with Se pellets at proper temperature. In a typical synthesis of SnSe nanoparticles, $SnCl_2$ (0.4 g), $W(CO)_6$ (0.1 g), HMDS (0.75 mL), OAm (10 mL), and ODE (90 mL) were mixed in a three-neck flask under the protection of Ar flow. The mixture was firstly heated to 60 °C and kept at this temperature for 10 min, then heated to 210 °C at a rate of 10 °C min⁻¹. The solution turned to brown black when up to 210 °C and held for 20 min. After cooled down to room temperature, the solution was vacuum degassed until no bubbles were generated and then filled with Ar gas. After injecting 4 mmol TOP-Se into the flask, the mixture was heated to 120 °C and held for 2 h. After cooled down to room temperature, the product was

separated and purified three times by adding hexane/ethanol through centrifugation.

Ligand removal: The as-prepared SnSe nanoparticles were dispersed into 20 mL n-butylamine and stirred for at least 12 h, and then was separated and purified several times by adding hexane/ethanol through centrifugation. At last, powder was obtained by drying the sediment under vacuum at 60 °C for at least 12 h. About 125 mg of SnSe powder can be obtained in one pot under this reaction condition.

Characterizations: X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Rigaku SmartLab) with Cu K α radiation (λ = 0.15418 nm) at a voltage of 45 kV and a current of 200 mA. Transmission electron microscope (TEM) images were captured by Tecnai F30 TEM (300 kV) and elemental mapping was obtained using Talos TEM (200 kV). TEM samples were prepared by placing a drop of the nanoparticle colloidal solution onto a carbon-coated Cu grid under ambient conditions. Scanning electron microscope (SEM) images of SnSe electrodes before and after long cycling were obtained by SEM (ZEISS, Merlin). Specific surface area was measured on an automated surface area analyzer (ASAP2420-4MP).

Electrochemical measurements: The electrochemical performance of as-prepared SnSe nanoparticles was assessed into CR2032 coin-type half cell using 16 mm Na disc as counter/reference electrode. The

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working electrode casted on Cu foil consists of the as-prepared powder, carbon black (Super P) and carboxymethyl cellulose (CMC) in a weight ratio of 6:2:2. The casted electrode was nature dried for 1 h followed by vacuum dried at 60 °C overnight. The working electrode is a disc with diameter of 16 mm and the typical loading of active materials is ~ 0.6 mg/cm². The separator is glass fiber and the electrolyte is 1.0 M NaPF_6 in digylme. Na₃V₂(PO₄)₃ (NVP) was used as a cathode in a full cell to couple with SnSe electrode. The mass ratio of positive electrode to negative electrode is about 6.38:1. The discharge-charge test was conducted using a Neware battery testing system under different rates within an operating voltage window of 0.01-3.0 V (vs. Na⁺/Na). The specific capacity was calculated based on the mass of the active material. CV curves were performed within a voltage window of 0.01-3.0 V at different scan rates. All tests were conducted at room temperature unless otherwise specified.



Fig. S1 (a) STEM image and (b) corresponding size distribution based on statistics collected over 200 particles of as-prepared SnSe nanoparticles.



Fig. S2 (a) Initial CV curve of SnSe electrode recorded with a scan rate of 0.1 mV/s. (b) Selected galvanostatic charge/discharge voltage profiles of SnSe electrode at 500 mA/g.

In the first cathodic scan, a broad peak observed between ~0.3 and ~0.8 V should be ascribed to formation of solid electrolyte interphase (SEI) layer, decomposition of SnSe (SnSe + $2Na^+$ + $2e^- \rightarrow Sn + Na_2Se$), and the partial alloying reaction of Sn with Na. The reaction peak lower ~0.3V should be originated from the further alloying reaction of Na_xSn (Na₁₅Sn₄ for complete sodiation).

As shown in Fig. 2c, SnSe electrode shows a capacity fluctuation upon cycling. The gradual increase of capacity at early cycles can be ascribed to the gradual activation of SnSe electrode; while the following decrease of capacity is originated from the gradual increase of the polarization (Fig. S2b), which is probably rooted from the gradual formation of stable but resistive SEI layer.



Fig. S3 (a) Schematic illustration to show the advantages of yolk-shell structured SnSe nanoparticles during sodiation/desodiation process. SEM images of SnSe electrode (b) before and (c) after 150 cycles at a current density of 500 mA/g.



Fig. S4 CV curves of SnSe electrode collected at different scan rates from 0.1 mV/s to 1.6 mV/s.



Fig. S5 (a) N_2 gas adsorption and desorption isotherm and (b) pore size distribution of as-prepared SnSe powders.

The N₂ gas-adsorption and desorption isotherms presented in Figure S5a contain clear hysteresis loop, which suggests type-H2 International Union of Pure and Applied Chemistry (IUPAC) isotherm classification. The Brunauer–Emmett–Teller (BET) surface area of the as-prepared SnSe nanoparticles is 42.7 m²/g. The pore size distribution derived from Barrett–Joyner–Halenda (BJH) method shows peaks between 3 nm and 7 nm, suggesting the existence of mesopores in as-prepared yolk-shell SnSe nanoparticles.

1 X. Zhao, Q. Di, X. Wu, Y. Liu, Y. Yu, G. Wei, J. Zhang and Z. Quan, *Chem. Commun.*, 2017, **53**, 11001-11004.