Supplementary Information

Yolk-shell $SnSe_2$@NC nanocubes: synergistic interior void and spatial confinement for superior sodium-ion battery anodes

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Experimental

1.1 Synthesis of $ZnSn(OH)_6$ composite precursor

In this study, a simple coprecipitation method was used to prepare the $ZnSn(OH)_6$ precursor. Under constant stirring, 2.875 g of $ZnSO_4 \cdot 7H_2O$ was dissolved into 50 mL deionized water to form solution A. Under constant stirring, 2.667 g of $Na_2SnO_3 \cdot 3H_2O$ was dissolved into 50 mL deionized water to form solution B. Then solution B was slowly added into solution A in a dropwise manner, resulting in a homogeneously blended milky-white solution. Subsequently, the mixture was continuously stirred at ambient temperature for 4 hours, leading to the formation of a milky-white precipitate. Finally, the sample was repeatedly washed with deionized water and ethanol and the white precipitate obtained by centrifugation was dried under vacuum at 70 °C for 12 h.

1.2 Synthesis of $ZnSn(OH)_6$@PDA

1 g of tris(hydroxymethyl)aminomethane was dispersed into 150 mL of mixed solution of water and ethanol with a volume ratio of 1:1 to prepare a buffer solution. Then 0.15g of $ZnSn(OH)_6$ precursor was dispersed into the buffer solution by ultrasonication for 0.5 h. Subsequently, 0.1 g of cetyltrimethylammonium bromide (CTAB), serving as a surfactant, was incorporated into the aforementioned solution under ultrasonication for 0.5 h. Then, 0.1 g of dopamine hydrochloride was added into the above solution, which was kept stirring for 24 h. The resultant product $ZnSn(OH)_6$@PDA was collected through centrifugation and washed several times with absolute ethyl alcohol and deionized water, respectively, and dried at 70 °C overnight.

1.3 Synthesis of $SnSe_2$ and $SnSe_2$@NC

The as-prepared $ZnSn(OH)_6$ and $ZnSn(OH)_6$@PDA were calcined at 600 °C for 7 h in Ar atmosphere, thereby yielding the calcined substance. Then the calcined product underwent an etching treatment using a 1 M HCl solution, with the aim of eliminating the impurity phase Zn_2SnO_4 to yield SnO_2 and SnO_2@NC. Subsequently, the prepared SnO_2 and SnO_2@NC and selenium powder (at a mass ratio of 1:8) were placed at the two extremities of a custom-made quartz tube and calcined at 450 °C for 4h under Ar/H_2 atmosphere (95% Ar： 5% H_2). Then the $SnSe_2$ and $SnSe_2$@NC composites were obtained. Schematic illustrations of preparation process for $SnSe_2$@NC are shown in Fig. 1.

1.4 Material characterizations

The crystalline phase and morphol-ogy of $SnSe_2$ and $SnSe_2$@NC comp-osites were investigated by powder X-ray diffractometry (XRD, BRUKER D8 ADV ANCE) with Cu-Kα radiation (λ=0.1540 6 nm) and scanning electron microscopy (SEM, SU8010). The microstructure of $SnSe_2$@NC composites was further identified by transmission electron micr-oscopy (TEM, America FEI Talos F200X). The valence states of $SnSe_2$@NC was analysed by X-ray photoelectron spectroscope (XPS, ESCALAB 250Xi).

1.5 Cell fabrication and characterization

The sodium storage performance of CR2025-type button battery was investigated by assembling the active substance of $SnSe_2$@NC. The $SnSe_2$ or $SnSe_2$@NC was fully ground in N-methylpyridone (NMP) with Ketjen Black and polyvinylidene fluoride (PVDF) binder at a mass ratio of 7:2:1 to obtain a slurry. The slurry was then evenly applied to copper foil and dried under vacuum at 90℃ for 12 h. Then the copper foil covered with the active substance is cut into a pole sheet with a diameter of 12.5 mm and weighed. The loading density of the active materials was 1.4 mg·cm-2. Electrochemical cells are assembled in an argon-filled glove box, in which O_2 and H_2O contents are below 0.01 ppm. The electrolyte is 1.0 M $NaSF_3SO_3$ in DIGYME (100% volume ratio), and sodium foil is used the anode and counter electrode. The glass fiber (GF/D, Whatman) was acted as the separator. The galvanostatic charge / discharge measurements are carried out in the voltage range of 0.01-3.0 V using a multichannel battery test system (LAND, CT2001A). Cyclic voltammetry (CV) and (EIS) for the prepared anodes are measured with a voltage window of 0.01-3.0 V on an electrochemical workstation (ChenHua CHI1040C). It is worth noting that all the specific capacities reported and current densities used here were based on the total mass of $SnSe_2$@NC.

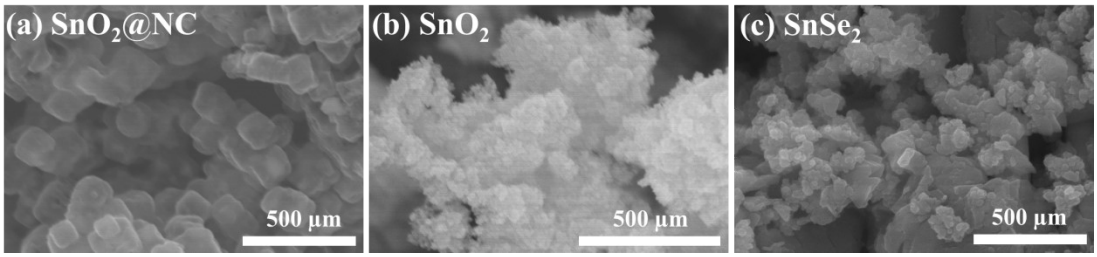

Fig. S1 SEM images of (a) SnO_2@NC, (b) SnO_2, (c) $SnSe_2$.

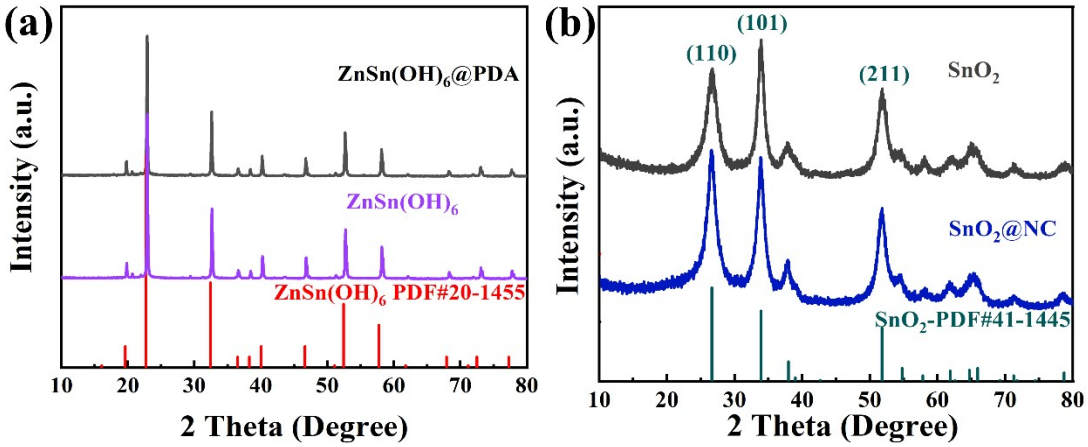

Fig. S2 (a) XRD patterns of $ZnSn(OH)_6$ and $ZnSn(OH)_6$@NC,

(b) XRD image of SnO_2 and SnO_2 materials after return processing.

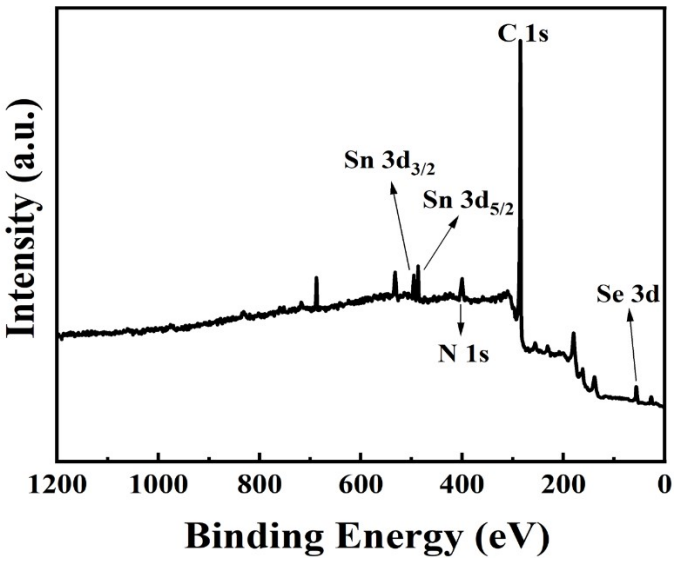

Fig. S3 XPS full spectrum of the $SnSe_2$@NC materials.

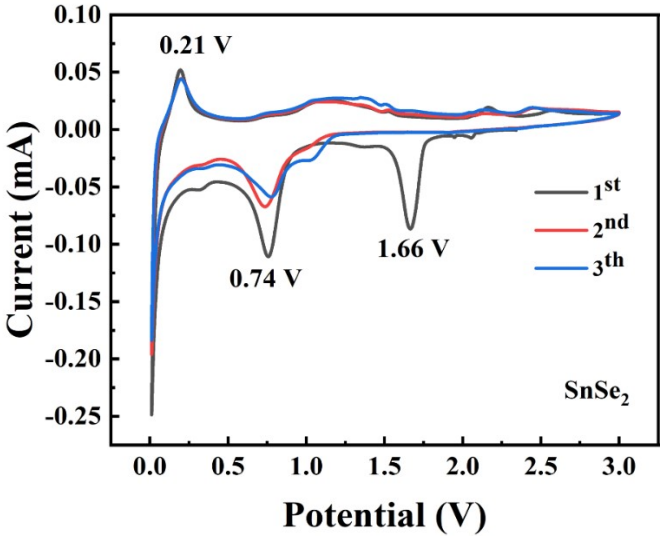

Fig. S4 CV curve of pure $SnSe_2$.

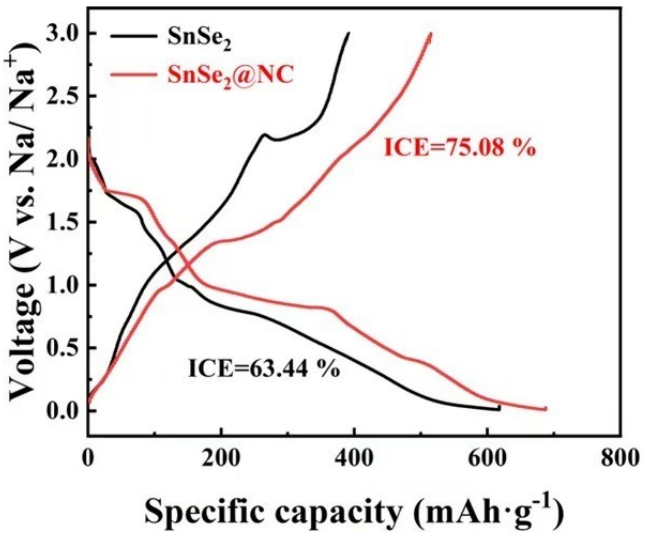

Fig. S5 Discharge/charge profiles for the first cycle of $SnSe_2$ and $SnSe_2$@NC electrodes.

Table S1 pure $SnSe_2$ and $SnSe_2$@NC: EIS fitting results of equivalent circuits

	R_s	R_{ct}
$SnSe_2$	19.88	127.8Ω
$SnSe_2$@NC	10.87	28.65

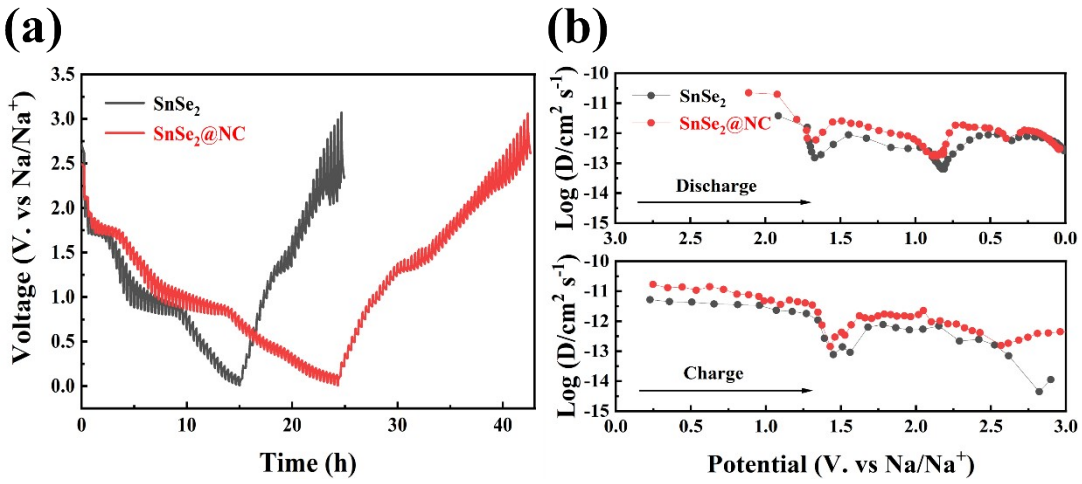

Fig. S6 (a)GITT voltage profiles of $SnSe_2$ and $SnSe_2$@NC electrodes; (b) Ion diffusion coefficient during the first Discharge/Charge process of $SnSe_2$ and $SnSe_2$@NC electrodes.