## **Supporting Information**

# Integrating Anti-Aggregation Ta-Se Motifs into Copper Selenide for Fast and Robust Sodium-Ion Storage

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## **Experimental Section**

### Synthesis of Cu<sub>3</sub>TaSe<sub>4</sub>

Cu<sub>3</sub>TaSe<sub>4</sub> was produced by one-step sintering using the solid-state method. Typically, the Cu, Ta and Se powders were ground and sealed in an evacuated quartz tube with a molar ratio of 3: 1: 4, which was placed into a muffle furnace with a heating rate of no more than 5 °C min<sup>-1</sup> until at 800 °C and kept for 12 hours. After natural cooling to room temperature, the product was ground in a mortar to obtain Cu<sub>3</sub>TaSe<sub>4</sub> sample powder.

## Characterization.

The X-ray diffraction (XRD) characterization was carried out on a Bruker D8 Advance diffractometer operating with a Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). Scanning

electron microscopy (SEM) images were obtained by a JEOL (JSM6510) scanning electron microscope. Transmission electron microscopy (TEM) observations were carried out on a JEOL (JEM-2100F) transmission electron microscope. Temperature-dependent resistivity measurement was conducted using a Physical Properties Measurement System (PPMS, Quantum Design). For the electrical property test, the sample powder was pressed into a square disc, and silver paste was used as the contact electrode. Raman spectroscopy was conducted on a Jobin-Yvon LabRAM HR-800 spectrometer with a laser excitation wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo Scientific Escalab 250 X-ray photoelectron spectrometer. The in situ XRD measurements was conducted using the operando battery cases at a constant current density of 50 mA g<sup>-1</sup>.

#### Battery assembly

All cells were assembled in an Ar-purified glovebox. The electrochemical performance was investigated by CR2032 coin type cells. The working electrode slurry was prepared by mixing the active material, conductive carbon black (Super P) and sodium alginate (SA) binder in a mass ratio of 8: 1: 1 with deionized water as the solvent. Then the slurry was coated evenly on a copper foil and dried under vacuum at 100 °C for 12 h. After that, the foil was punched into 12 mm discs. The average mass loading of the active material on each disc is 1.0-1.2 mg cm<sup>-2</sup>. The half cells were assembled with sodium disc (Canrd, 99.7%, 15.6\*0.45mm) as the counter electrode and glass fiber (GF/D, Whatman) as the separator in an argon-filled glove box (MBRAUN-LABstar, with H<sub>2</sub>O and O<sub>2</sub> levels < 0.5 ppm). The electrolyte was 1.0 M NaPF<sub>6</sub> in diethylene glycol dimethyl ether (DIGLYME) = 100 Vol%. The specific capacity of the half cell was calculated based on the total mass of anode. The cells were left standing for 8 h before measurements to guarantee full contact between the electrolyte and active materials.

Electrochemical measurements

Galvanostatic charge/discharge galvanostatic intermittent titration technique (GITT) measurements were performed on a cell test system (LAND-CT2001A) in the voltage range of 0.01-3 V. The GITT was performed through a pulse current of 40 mA g<sup>-1</sup> for 10 min followed by relaxation intervals of 40 min. Cyclic voltammogram (CV) from 0.01 to 3.0 V and electrochemical impedance spectroscopy (EIS) over the frequency from 100 kHz to 0.1 Hz were measured by CHI760E electrochemical workstation (Chenhua, Shanghai).

Theoretical capacity calculations.

The theoretical capacity (1 C = 311.9 mA  $g^{-1}$ ) is calculated according to the following formula:

$$C_{t} = \frac{nF}{3.6M_{r}}$$

Where n is the number of transferred electrons, F is the Faraday constant (96485 C mol<sup>-1</sup>), and Mr is the molar mass of Cu<sub>3</sub>TaSe<sub>4</sub> (687.4 g mol<sup>-1</sup>). Sodium intercalation reaction of Cu<sub>3</sub>TaSe<sub>4</sub>: Cu<sub>3</sub>TaSe<sub>4</sub> + 8Na<sup>+</sup> + 8e<sup>-</sup>  $\rightarrow$  3Cu + Ta + 4Na<sub>2</sub>Se

Carrier concentration calculations.

The carrier concentration *n* is calculated according to the following formula:

$$Slope = \frac{R_{hall}}{B} = \frac{W_e}{DqW_s} \frac{1}{n}$$

Where  $R_{hall}$  is the Hall resistance of the sample, *B* is the magnetic flux density,  $W_e$  is the distance between electrodes,  $W_s$  is the width of the sample, *D* is the height of the sample along the direction of *B*, and *q* is the charge of the carrier (1.6×10<sup>-19</sup> C).

Diffusion coefficient calculations.

According to Fick's second law and Faraday's law, the classical diffusion coefficient is calculated as follows:

$$D = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{SM_B}\right)^2 \cdot \left(\frac{\Delta E_s}{\Delta E_t}\right)^2$$

Where  $m_B$  and  $M_B$  represent the mass and molar mass of the electrode material, respectively, S denotes the electrode-electrolyte contact area,  $V_M$  is the molar volume of the electrode material,  $\Delta E_s$  is the change in the steady-state voltage, and  $\Delta E_t$  refers to the voltage change in a single step Galvanostatic Intermittent Titration Technique (GITT) experiment.

Anode	Rate capacity <sup>a)</sup>	Cycling stability <sup>a,b)</sup>	Reference
Cu <sub>2</sub> Se	$99 @ 2 A g^{-1}$	101 (2000) @ $2 \text{ A g}^{-1}$	[1]
h-CuSe	$210 @ 15 A g^{-1}$	220 (1000) @ $3 \text{ A g}^{-1}$	[2]
Cu@SnSe	$330 @ 20 A g^{-1}$	$304 (1000) @ 5 A g^{-1}$	[3]
Fe7Se8@C@MoSe2	$274 @ 5 A g^{-1}$	345 (600) @ $1 \text{ A g}^{-1}$	[4]
Cu4Mo6Se8@C	$365 @ 5 A g^{-1}$	474 (2400) @ 2 A $g^{-1}$	[5]
NiCo <sub>2</sub> Se <sub>4</sub>	$220 @ 5 A g^{-1}$	230 (2500) @ 5 A $g^{-1}$	[6]
Cu <sub>2</sub> Se@ZnSe	$237 @ 2 A g^{-1}$	205 (500) @ $0.5 \mathrm{A}\mathrm{g}^{-1}$	[7]
Cu <sub>3</sub> TaSe <sub>4</sub>	$286 @ 15 A g^{-1}$	272 (3500) @ 6 A g <sup>-1</sup>	This work

 Table 1. Sodium storage performance comparison of advanced SIB selenide anodes

 and Cu<sub>3</sub>TaSe<sub>4</sub>.

a) Capacity unit is mAh  $g^{-1}$ ; b) Cycling number is in the bracket.



Fig. S1 Lower magnification SEM images of Cu<sub>3</sub>TaSe<sub>4</sub>.



Fig. S2 XPS Survey spectrum of Cu<sub>3</sub>TaSe<sub>4</sub>.



Fig. S3 High-resolution XPS spectra of Se 3d in Cu<sub>3</sub>TaSe<sub>4</sub>.



Fig. S4 Rate capability and of Cu<sub>3</sub>TaSe<sub>4</sub> under different mass loadings.



Fig. S5 (a) XRD pattern, (b) SEM, (c) EDS images of Cu2Se.



Fig. S6 (a) GCD curves of Cu<sub>2</sub>Se in the initial three cycles. (b) Rate performance of Cu<sub>3</sub>TaSe<sub>4</sub> and Cu<sub>2</sub>Se. (c) CV curves of Cu<sub>2</sub>Se in the initial three cycles. (d) GITT potential profiles of Cu<sub>2</sub>Se and Corresponding Na<sup>+</sup> diffusion coefficients (D<sub>Na<sup>+</sup></sub>) during discharge–charge.



Fig. S7 Cycling performance of  $Cu_3TaSe_4$  at current density of 1 C.



Fig. S8 Pseudo-capacity contributions of the  $Cu_3TaS_4$  anode at a) 0.4 mV s<sup>-1</sup>, b) 0.6 mV s<sup>-1</sup>, c) 0.8 mV s<sup>-1</sup>, d) 1.0 mV s<sup>-1</sup>, and e) 1.5 mV s<sup>-1</sup>.



Fig. S9 Voltage response over time during a single current pulse in GITT.



Fig. S10 In situ XRD stacking diagram of Cu<sub>3</sub>TaSe<sub>4</sub> during the first cycle.

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