Supplementary material for

Immobilizing and boosting lithium polyselenides conversion via a WSe$_2$/WO$_2$
 heterostructure engineering strategy for lithium selenium batteries

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This profiles contains the experimental section, and supplementary (Figs S1 to S19, and Tabs S1 to S2).
1. Experimental section

1.1 Material

The commercial WO₃ powder (99.8% purity), ethylenediamine (EDA, AR), selenium (Se) powder (99.9% purity) and multi-walled carbon nanotube (CNT, ≥95% purity) were purchased from Aladdin, Xilong Scientific, Macklin and Macklin, respectively. These commercial materials were used without further purification.

1.1.1 Preparation of W₅O₁₄⁻EDA nanorod precursor

The W₅O₁₄⁻EDA nanorod precursor was synthesized through a solvothermal reaction according to previous reports.¹ In a typical procedure, the WO₃ powder (800 mg) was dispersed into 60 mL EDA, and the mixture was treated by ultrasonication for 60 min. Then the suspension was transferred into a Teflon-lined sealed autoclave, which was heated at 180 °C for 12 hours. The sediment was rinsed by centrifugation with the mixture of deionized water and ethanol after the autoclave natural cooling, and it was vacuum dried at 60 °C for 18 hours to obtain the white precursor product of W₅O₁₄⁻EDA nanorods.

1.1.2 Preparation of nanosheet on nanorod WSe₂/WO₂ heterostructure

The nanosheet on nanorod WSe₂/WO₂ heterostructure was prepared by an in-situ selenization method. In detail, W₅O₁₄⁻EDA nanorod precursor was placed at the downstream and Se powder was placed at the upstream of a tube furnace. The precursor was calcinated at 600 °C for 3 hours in the mixed flow of 5% H₂ and 95% Ar. By adjusting the mass ratio of Se and W₅O₁₄⁻EDA nanorod (from 0:1, to 1:10, 1:1 and 10:1), the WSe₂/WO₂ heterostructure with varied weight ratio between WSe₂ and WO₂
was received, which were abbreviated as “WSe$_2$/WO$_2$(0:1), WSe$_2$/WO$_2$(1:10), WSe$_2$/WO$_2$(1:1), WSe$_2$/WO$_2$(10:1)”. It is noted that the subscripts of \((n:m)\) represent the weight ratio between Se powder and W$_5$O$_{14}$-EDA nanorod precursors.

1.2 Electrochemical property measurements

1.2.1 Preparation of the selenium cathodes and the selenium-free cathodes

To disperse the electrode material evenly, 60 mg (or 10 mg) CNT and 40 mg (or 90 mg) selenium powder were dispersed in 100 mL ethanol under the ultrasonic, and then drying at 60 °C in an oven for 12 hours. The mixture was transferred to a vacuum self-sealing glass tube, which was heated at 260 °C for 12 hours to obtain the Se@CNT composite. The cathodes were fabricated by grinding and coating the slurries of 80 wt.% Se@CNT, 10 wt.% carbon black, 10 wt.% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) on Al foil and drying at 60 °C for 18 hours in a vacuum oven. The selenium loading on the cathode is around 1.0 mg cm$^{-2}$. Selenium-free materials were employed as the cathode for the measurement of reaction kinetics. A homogeneous slurry was obtained by mixing 80 wt.% CNT, 10 wt.% carbon black and 10 wt.% PVDF in NMP, which was then uniformly coated on Al foil, and dried at 60 °C in a vacuum oven for 12 hours to obtain selenium-free electrodes.

1.2.2 Preparation of modified separator

The modified separator was prepared using a facile slurry-coating method. 40 wt.% of WSe$_2$/WO$_2$(0:1) (or WSe$_2$/WO$_2$(1:10), WSe$_2$/WO$_2$(1:1), WSe$_2$/WO$_2$(10:1)) 40 wt.% of CNT, 10 wt.% carbon black, and 10 wt.% PVDF were vigorously grinded together in NMP solvent to fabricate a homogeneous slurry, which was coated on pristine Celgard 2500
(PP) separator. Then, the modified separator was dried in a vacuum oven at 60 °C for 12 hours. Subsequently, the functionalized separator was cut into discs with a diameter of 19 mm.

1.2.3 Lithium polyselenide (Li$_2$Se$_6$) solution and visualized adsorption test

Li$_2$Se$_6$ solution (0.5 mol L$^{-1}$) was prepared by dissolving Se and Li$_2$Se (5:1 mol%) in a mixed solvent of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 vol%) under strong magnetic stirring and heating. Then 10 mg CNT and 10 mg WSe$_2$/WO$_2$ were added into 1 mL Li$_2$Se$_6$ solution. The ex-situ ultraviolet-visible (UV) absorption spectra of the extracting top liquid was conducted after 48 hours resting.

The H-type electrolytic tanks were assembled to test the polyselenides-blocking capability of modified separator. 3 mL DME was added into the left side and 3 mL 0.5 mol/L Li$_2$Se$_6$ solution was added into the right side. The ex-situ ultraviolet-visible (UV) absorption spectra of the extracted left liquid was conducted after resting 34 h. The above measurements were carried out in argon glove box.

1.2.4 Assemble and test of Li$_2$Se$_6$ symmetrical cells

The electrodes were prepared by grinding and coating slurry of active material (CNT), carbon black and PVDF with a mass ratio of 8:1:1 in NMP solvent on Al foils, which were dried in a vacuum oven at 120 °C for 12 hours. 0.1 M Li$_2$Se$_6$ electrolyte was prepared by intensively stirring selenium powder and lithium selenide (5:1 mol%) in the electrolyte (1M LiTFSI in DME/DOL (1:1 vol%)) under heating. The selenium-free electrodes were used as working electrode and counter electrode of the symmetrical cell, and 40 μL of 0.1 M Li$_2$Se$_6$ was used as electrolyte. The CV tests of the symmetric
cells, which were equipped with two different separators (pristine PP separator and 
WSe$_2$/WO$_2$ modified separator), were measured in a voltage range of from -1.5 V to 
1.5 V at a sweep rate of 10 mV/S.

1.2.5 Li$_2$Se nucleation measurements

To investigate the liquid-solid conversion kinetics, 0.5 M Li$_2$Se$_6$ solution was prepared 
by mixing Se and Li$_2$Se (molar ratio of 5:1), which were dissolved in the mixture 
solution of DME and DOL (1:1 vol%) containing 1.0 M LiTFSI under heating with 
vigorous stirring. Lithium foil was served as anode and two kinds of membranes were 
served as separators, respectively. 20 µL of Li$_2$Se$_6$ (0.5 M) was dropped onto the 
cathode, and 20 µL of traditional LiTFSI electrolyte was dropped to the anode. The 
batteries were discharged galvanostatically at 0.1 mA to 2.00 V and kept potentiostatic 
at 2.00 V for Li$_2$Se to nucleate until the current reduced below 0.01 mA. The nucleation 
capability of Li$_2$Se can be assessed by the integral area of the curve through Faraday’s 
Law.

1.2.6 Electrochemical performances of Li-Se batteries

The electrochemical properties of the selenium cathode (the Se@CNT cathode) were 
evaluated by CR-2032 coin-type cells equipped lithium foil as the anodes, pristine PP 
membrane (or WSe$_2$/WO$_2$ membrane) as a separator, DME/DOL (1:1 vol%) solution 
containing 1.0 M LiTFSI and 1 wt.% lithium nitrate (LiNO$_3$) as the electrolyte. The 
assemble of coin-type cells was conducted in an argon glove box with the contents of 
oxygen and water below 0.1 ppm. The galvanostatic charge/discharge test was 
measured on a LAND CT2001A system in a range of voltage from 1.0-3.0 V under
different C-rates (1 C = 675 mAh g⁻¹). The CV measurements and electrochemical impedance spectroscopy (EIS) measurements within the frequency range of 0.01-10⁵ Hz were tested on an Autolab electrochemical workstation. The above electrochemical tests were experimented at the room temperature (25°C). The performances of Li-Se batteries with pristine PP separators are characterized under varied selenium/electrolyte ratios. The performances of Li-Se batteries with varied coating materials modified PP separators are characterized. The performances of Li-Se batteries with WSe₂/WO₂(1:10) modified separator with varied coating thickness are also investigated.

1.3 Material Characterizations

The product’s morphology was characterized using a field emission scanning electron microscopy (FESEM, JSM-6700F) at an accelerating voltage of 8 kV, and a high-resolution transmission electron microscopy (HRTEM, JEM-2100F) equipped with an EDX spectrometer. The crystal structure of the product was detected by X-ray diffraction (XRD, D/MAX/2500PC) with Cu Kα radiation (λ=1.5406 nm) at a scan rate of 20°/min. A Thermo Scientific ESCALAB 250Xi electron spectrometer manifested the X-ray photoelectron spectroscopy (XPS) of the material. Raman spectroscopy (Lab RAM HR Evolution) was measured with 633nm excitation wavelength, operated in the range of 100-1800 cm⁻¹. The thermogravimetric (TG) was carried out using a TGA 5500 in order to test the content of carbon in the heterostructure heating from 30 °C to 500 °C in air. The thermogravimetric (TG) was intended to test the content of Se in the Se@CNT heating from 30 °C to 800 °C in a nitrogen atmosphere.
1.4 Theoretical modelling

The density functional theory (DFT) calculations have operated within the generalized gradient approximation (GGA) employed the Perdew-Burke-Ernzerhof (PBE) according to the first-principles. The projected augmented wave (PAW) potentials were chosen to elaborate the ionic cores and valence electrons were took into account employing a plane wave basis which is cutoff at 520 eV kinetic energy. Basing on Gaussian smearing method, it allows partial occupancies of the Kohn-Sham orbitals, which are 0.05 eV width. When the energy change belows than $10^{-6}$ eV, it regards as the electronic energy is self-consistent. And when the energy change is inferior to 0.03 eV Å$^{-1}$, it deems that a geometry optimization is convergent. In our structure, the W atoms were amended by U correction. In a direction vertical to the plane in the structure, the vacuum spacing is 20 Å. Using $3\times3\times1$ Monkhorst-Pack k-point sampling, the Brillouin zone integration was carried out for a structure. Ultimately, the adsorption energies (Eads) were computed via a formulation ($E_{\text{ads}} = E_{\text{ad/sub}} - E_{\text{ad}} - E_{\text{sub}}$), which $E_{\text{ad/sub}}$, $E_{\text{ad}}$, and $E_{\text{sub}}$ are correspond to the general energies of optimized adsorbate/substrate system, the adsorbate of structure, and the pure substrate, respectively. The free energy was computed according the equation:

$$G = E_{\text{ads}} + \text{ZPE-TS}$$

where $G$ is the free energy, $E_{\text{ads}}$ is total energy from DFT calculations, ZPE is zero point energy, and TS is entropic contributions. Using the Climbing Image-Nudged Elastic Band methods, the energy barriers were calculated for the structure.
Fig. S1 (a) The SEM image and (b) The XRD spectra of W$_5$O$_{14}$-EDA nanorod precursor.

Fig. S2 cycle performance (a) and the capacity of the 50th cycle (b) at 1 C adding different electrolyte dosages.
**Fig. S3** cycle performance (a) and the capacity of the 50th cycle (b) at 1 C modified by 10 μm different selenization degree products coating using 1/15 electrolyte dosage.

**Fig. S4** The initial charge and discharge profiles of different separators with 72 wt.% Se content.

**Tab. S1** The thickness and loading of WSe$_2$/WO$_2$(1:10) diaphragm coating.

<table>
<thead>
<tr>
<th>Thickness (μm)</th>
<th>5 μm</th>
<th>10 μm</th>
<th>15 μm</th>
<th>20 μm</th>
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<tr>
<td>$m_{\text{WSe}_2/\text{WO}_2}$ (mg)</td>
<td>0.172</td>
<td>0.344</td>
<td>0.488</td>
<td>0.620</td>
</tr>
<tr>
<td>Loading (mg/cm$^2$)</td>
<td>0.086</td>
<td>0.171</td>
<td>0.243</td>
<td>0.309</td>
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</tbody>
</table>

**Tab. S2** This work is compared with other literatures on the degree of overcharge, Se content and Se loading.

<table>
<thead>
<tr>
<th></th>
<th>CP/Se</th>
<th>CMK-3/Se$_3$S$_3$</th>
<th>CB/Se</th>
<th>FMG/Se</th>
<th>This wok</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se loading/(mg cm$^{-2}$)</td>
<td>1.0</td>
<td>1.25</td>
<td>1.8</td>
<td>2.25</td>
<td>1.0</td>
</tr>
<tr>
<td>Overcharge/(mAh g$^{-1}$)</td>
<td>311</td>
<td>979</td>
<td>34</td>
<td>131</td>
<td>28.3</td>
</tr>
<tr>
<td>Se wt.%</td>
<td>80</td>
<td>34.3</td>
<td>60</td>
<td>22.2</td>
<td>32</td>
</tr>
<tr>
<td>Current density (A g$^{-1}$)</td>
<td>0.337</td>
<td>0.0675</td>
<td>0.0675</td>
<td>0.05</td>
<td>0.675</td>
</tr>
</tbody>
</table>
Cycle performances (mAh g\(^{-1}\) after 50 cycles)

<table>
<thead>
<tr>
<th></th>
<th>310</th>
<th>240</th>
<th>230.6</th>
</tr>
</thead>
</table>

CP/Se is 311 mAh g\(^{-1}\) overcharged at 0.5 C, employed 80 wt.% selenium content, 1.0 mg cm\(^{-2}\) selenium loading.\(^7\) CB/Se is 34 mAh g\(^{-1}\) overcharged at 0.1 C, employed 60 wt.% selenium content, 1.8 mg cm\(^{-2}\) selenium loading.\(^8\) CMK-3/Se\(_2\)S\(_3\) is 979 mAh g\(^{-1}\) overcharged at 0.067 A g\(^{-1}\), employed 34.3 wt.% selenium content, 1.25 mg cm\(^{-2}\) selenium loading.\(^9\) FMG/Se is 131 mAh g\(^{-1}\) overcharged at 0.05 A g\(^{-1}\), employed 22.2 wt.% selenium content, 2.25 mg cm\(^{-2}\) selenium loading.\(^10\)

**Fig. S5** The N\(_2\) adsorption/desorption curve (a) and pore size distribution (b) of CNT.
Fig. S6 (a) The XRD pattern of Se@CNT, Se, and CNT; (b) The SEM image of Se@CNT; (c) TG curve of Se@CNT.

Fig. S7 The charge and discharge profiles of WO$_2$ (a) and WSe$_2$ (b) at 0.5 A g$^{-1}$ within a voltage window of 0-3.0 V.
Fig. S8 (a) Cycling performances and Coulombic efficiency of Li-Se batteries with WSe$_2$/WO$_2$ separator and PP separator at 0.2 C; The charge and discharge profiles of different separators at 1$^{st}$ cycle (b) 2$^{nd}$ cycle (c); (d-g) The enlarged details of the galvanostatic charge/discharge profiles of Li-Se batteries with varied separators.

As shown in Fig. S8a, the Li-Se battery with WSe$_2$/WO$_2$ modified separator displays a considerable discharge capacity of 969 mAh g$^{-1}$ in the first cycle and retains a superior capacity (270 mAh g$^{-1}$) after 50 cycles at 0.2 C, while the Li-Se batteries with pristine PP separator show an inferior discharge capacity of 668 mAh g$^{-1}$ in the first cycle and only retains a lower capacity of 183 mAh g$^{-1}$ after 50 cycles at 0.2 C. In addition, the Coulombic efficiency (Fig. S8a) of Li-Se batteries with WSe$_2$/WO$_2$ separator is approaching 100%, while for the Li-Se batteries with PP separator there is an obvious overcharge behaviour (Coulombic efficiency is significantly higher.). The accumulated heat from overcharging might affect the battery safety. As shown in Fig. S8b, the Li-Se batteries with WSe$_2$/WO$_2$ modified separator show less overcharge capacity compared to that with pristine PP separator. As for Li-Se battery with WSe$_2$/WO$_2$ modified separator, the charge profile shows a lower initial charging voltage (1.0201
V) than that with PP separator (1.0212 V) (Fig. S8c). Also, it also shows a lower recharge overpotential (2.1838 V) than that with PP separator (2.2046 V) (Fig. S8d). These results manifest the potential energies needed for the transformation of LiPSes and the decomposition of Li₂Se are markedly decreased with WSe₂/WO₂ modified PP separator. The lower discharge overpotential of Li-Se battery with WSe₂/WO₂ separator (2.034 V) can be detected compared to that with PP separator (2.0213 V) (Fig. S8e), which indicates that the energy needed for the liquid to solid transformation of Li₂Se₆ to Li₂Se₄ is notable reduced. From Fig. S8f, a polarization potential gap of 114.3 mV can be detected in the charge and discharge curves of Li-Se battery with WSe₂/WO₂ separator, which is lower than that with PP separator (123.4 mV).

![Fig. S9](image)

Fig. S9 The charge-discharge profile of the 10th cycle with varied separators at 1 C.
Fig. S10 The cycling performances of Li-Se batteries at 0.8 C.

Fig. S11 The impedance patterns of batteries with WSe$_2$/WO$_2$(1:10) separator and PP separator at diversified conditions.

Fig. S12 The rate performances of the Li-Se batteries with PP separator and WSe$_2$/WO$_2$ modified separator within a voltage window of 1.0-3.0 V.
The lower capacity at 1C in Fig. S12 (rate tests) than in Fig. 4a (cycle performance tests) is attributed to the self-discharge issues in Li-Se batteries. The specific capacity at 1C after rate performance test (around 20 cycles) is determined to be 268.3 mAh g⁻¹ (Fig. S12), while it is about 340.9 mAh g⁻¹ after cycle performance test (after 20 cycles) (Fig. 4a). It is obvious that the former is less than the latter capacity. It is worth noting that the unavoidable dissolution and shuttle of lithium polyselenides can lead to the gradual capacity degradation during electrochemical performance tests. The much longer time for the rate performances test can induce a faster capacity decay than the cycle performance test, which is responsible for the lower capacity.

Fig. S13 The performance comparison with a mesoporous CMK-3 host.
Fig. S14 The rate performances of the Li-Se batteries with WSe$_2$/WO$_2$ modified separator and PP separator within a voltage window of 1.7-2.6 V.

Fig. S15 Digital photographs of LEDs contacting with Li-Se batteries (a) PP separator; (b) WSe$_2$/WO$_2$ separator.
Fig. S16 Digital photos of lithium anodes and separators of Li-Se batteries with PP separator (a) and WSe$_2$/WO$_2$ separator (b) at different states.

Fig. S17 Adsorption experiments after 40 h soaking.
Fig. S18 The substance structures in discharge conversion on various surfaces.
Fig. S19 (a) Optimized geometry of WOE precursor; (b) Optimized geometry of WO$_2$; (c) Optimized geometry of WSe$_2$. 

(c) Optimized geometry of WSe$_2$. 

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References