Supplementary Information

Se vacancies-rich VSe$_2$ nanosheets with carbon-free for high-performance lithium storage

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Materials characterizations: The obtained products were characterized on a powder X-ray diffraction (XRD) (Bruker D8 X-ray power diffractometer) operated at 40 kV voltage and 50 mA current. XRD pattern was recorded from 10° to 80° (2θ) with a scanning step of 10°/min. The morphologies of the products were examined by field emission scanning electron microscopy (FESEM, HITACHI S-4800) and transmission electron microscopy (TEM, JEOL JEM-2010). The Brunauer-Emmett-Teller (BET) specific surface areas of typical products were performed at 77 K in a Belsorp-max surface area detecting instrument. Raman spectra were recorded at Renishaw Invia Raman spectrometer, using an excitation laser of 633 nm. The photoluminescence (PL) spectra were obtained by using a Cary Eclipse fluorescence spectrometer (Varian, USA) with Xe lamp as the excitation source. Positron annihilation lifetime spectroscopy (PALS) was performed by a conventional fast-low coincidence spectroscopy. The time resolution was 195 ps at room temperature, and 16 μCi ²²Na was used as the positron source. The X-ray absorption near edge structure (XANES) measurements were undertaken at Beamlines 1W1B at Beijing Synchrotron Radiation Facility (BSRF) using transmission and fluorescence modes.

Electrochemical measurements: The electrochemical tests were performed at room temperature by using coin cells (CR2025) on LAND CT2001A with a cutoff voltage of 0.01–3.00 V vs. Li⁺/Li. The samples obtained above were used as active materials. For the anode preparation, the active material, conductive carbon black, and sodium carboxymethyl cellulose (CMC) with a mass ratio of 70:20:10 were mixed and ground
in a mortar. Deionized water was used as the solvent to make homogeneous slurry. The as-resultant slurry was uniformly pasted on a Cu foil and dried at 120 °C for 24 h in a vacuum oven. The cell assembly was performed in an Ar-filled glove box. The loading of the active material was about 0.8 mg cm\(^{-2}\). The used electrolyte was 1 M LiPF\(_6\) dissolved in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1, in vol\%). A lithium foil was used as counter electrode. Cyclic voltammetry (CV) was measured by a CHI-760E electrochemical workstation with a scan rate of 0.1 mV s\(^{-1}\). The impedance spectra were obtained by applying a sine wave with amplitude of 5 mV over the frequency range from 100 kHz to 0.01 Hz. To collect the active materials after cycling for the measurements of XRD, the electrodes were disassembled from the cells in an Ar-filled glove box, and then rinsed with absolute alcohol and DMC (Sigma-Aldrich, 99%) to remove the residual electrolyte.

**Calculations of the capacitive contribution and diffusion-limited contribution:**

To quantitatively distinguish the capacitive and diffusion-controlled contributions to current, CV curves at a series of sweep rates were tested. Generally, the relationship between the measured peak current \(i\) and sweep rate \(v\) in a CV scan follows the following formula:

\[
i = av^b
\]

then, \(\log(i) = \log(a) + b \cdot \log(v)\)

Apparently, the b value can be obtained by fitting slope of the log(i) versus log(v) profile. When the b value is 0.5, it demonstrates a diffusion-controlled behavior, while
the b value of 1.0 corresponds to a capacitive behavior. The capacitive contribution and diffusion-controlled contribution can be further quantitatively distinguished assuming that the current ($i$) is a combination of the capacitor-like and diffusion-controlled processes according to:

$$i = k_1 v + k_2 v^{1/2}$$

We can calculate the capacitive and diffusion limited contributions by determining $k_1$. 
**Fig. S1** (a) Low-magnification and (b) high-magnification SEM images of VSe$_2$-NSs.

**Fig. S2** (a) Low-magnification and (b) high-magnification SEM images of bulk VSe$_2$. 
**Fig. S3** (a) N$_2$ adsorption-desorption isotherms and (b) corresponding pore size distribution of bulk VSe$_2$.

![Graph showing N$_2$ adsorption-desorption isotherms and pore size distribution of bulk VSe$_2$.](image)

**Fig. S4** Raman spectrum of VSe$_2$-NSs.

![Graph showing Raman spectrum of VSe$_2$-NSs.](image)
Fig. S5 CV curves of the bulk VSe$_2$ for the first three cycles at a scan rate of 0.1 mV s$^{-1}$.

![Graph showing CV curves for the first three cycles of bulk VSe$_2$ at a scan rate of 0.1 mV s$^{-1}$]

Fig. S6 Cycle performance of VSe$_2$-NSs at various temperatures at 0.1 A g$^{-1}$.

![Graph showing cycle performance of VSe$_2$-NSs at various temperatures at 0.1 A g$^{-1}$]
Fig. S7 (a,b) SEM images of VSe$_2$-NSs-6h. (c) XRD pattern of VSe$_2$-NSs-6h and VSe$_2$-NSs. (d) Cycling performance of VSe$_2$-NSs-6h and VSe$_2$-NSs at 0.1 A g$^{-1}$.

Table S1. Positron lifetimes and relative intensities of VSe$_2$-NSs-6h and VSe$_2$-NSs.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\tau_1$ (ps)</th>
<th>$I_1$ (%)</th>
<th>$\tau_2$ (ps)</th>
<th>$I_2$ (%)</th>
<th>$\tau_3$ (ns)</th>
<th>$I_3$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VSe$_2$-NSs-6h</td>
<td>164.7 ± 5.2</td>
<td>37.3 ± 1.5</td>
<td>332.6 ± 3.9</td>
<td>60.8 ± 1.5</td>
<td>2.197 ± 0.047</td>
<td>1.895 ± 0.069</td>
</tr>
<tr>
<td>VSe$_2$-NSs</td>
<td>181.2 ± 4.4</td>
<td>59.4 ± 1.3</td>
<td>357.5 ± 3.1</td>
<td>38.7 ± 1.2</td>
<td>2.289 ± 0.044</td>
<td>1.871 ± 0.062</td>
</tr>
</tbody>
</table>
**Fig. S8** (a) The b-values of different redox peaks. (b) CV curves of VSe$_2$-NSs at different scan rates.