Supporting Information

Hierarchical Nanoarchitectured Hybrid Electrodes Based on Ultrathin MoSe$_2$ Nanosheets on 3D Ordered Macroporous Carbon Frameworks for High-Performance Sodium-Ion Batteries

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**Experimental Section**

**Synthesis of 3DOM MoO\(_2\)@C framework**

The 3DOM MoO\(_2\)@C framework was synthesized via a template route using silica spheres as the template obtained by Stober's method (Figure S1). First, The SiO\(_2\) nanospheres, polyvinylidene fluoride (PVDF) and Bis(acetylacetonato)-dioxomolybdenum(VI) (MoO\(_2\)(acac)\(_2\)) were dispersed in NMP solution at appropriate proportion, and then, dried at 80 °C overnight to get a well-mixed mixture. The mixture calcined at 500 °C for 2 h in N\(_2\) atmosphere to convert PVDF into carbon materials, MoO\(_2\)(acac)\(_2\) into MoO\(_2\). Afterwards, the resultant product was immersed in HF solution for 24 h to remove SiO\(_2\) template, resulting in 3DOM MoO\(_2\)@C framework formation.

**Synthesis of 3DOM MoSe\(_2\)@C**

In a typical procedure for 3DOM MoSe\(_2\)@C, Selenium (0.316 g) was dissolved in 10 ml hydrazine hydrate followed by adding the MoO\(_2\)@C (0.472 g) and 50 ml deionized water to form a black suspension under intensively magnetic stirring at room temperature. The as-prepared suspension transferred into Teflon-lined stainless-steel autoclave with 80 mL and kept at 200 °C for 24 h. After cooling naturally, the power was collected by filtered and washed with deionized water and
absolute ethyl alcohol several times, and subsequently dried at 80 °C overnight, forming 3DOM MoSe\textsubscript{2}@C (MSC). The obtained MSC was further calcined in N\textsubscript{2} atmosphere at 600 °C for 5 hours to combine carbon and molybdenum selenide more tightly, producing calcined MSC (C-MSC). The pristine MoSe\textsubscript{2} (MS) was prepared by Na\textsubscript{2}MoO\textsubscript{4} rather than MoO\textsubscript{2}@C via the same hydrothermal process of MSC.

**Synthesis of 3DOM MoP@C:**
In this general phosphating process, the MoO\textsubscript{2}@C and NaH\textsubscript{2}PO\textsubscript{2} were put into a tube furnace for calcination at a weight ratio of 1: 10, among that, the NaH\textsubscript{2}PO\textsubscript{2} at upstream under H\textsubscript{2} (5%)/Ar\textsubscript{2} atmosphere keeping 2 h at 800 °C with the heating rate of 5 °C/min. After cooling down to room temperature, the MoP@C was obtained.

**Synthesis of 3DOM MoS\textsubscript{2}@C**
The synthetic procedure of 3DOM MoS\textsubscript{2}@C is the same as 3DOM MoSe\textsubscript{2}@C except change selenium into sulfur.

**Synthesis of 3DOM Mo\textsubscript{2}C@C**
The synthesis of 3DOM Mo\textsubscript{2}C@C is also very similar to that of 3DOM MoS\textsubscript{2}@C. The difference is calcination of 3DOM MoO\textsubscript{2}@C in hydrogen at 500 °C for 2 h. After naturally cooling down to room temperature, the black powder is 3DOM Mo\textsubscript{2}C@C.

**Synthesis of Na\textsubscript{3}V\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}/C:**
The Na\textsubscript{3}V\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}/C (NVP/C) was synthesized according to the work by Yang et al.\textsuperscript{60} The NH\textsubscript{4}VO\textsubscript{3}: NaH\textsubscript{2}PO\textsubscript{2}: C\textsubscript{6}H\textsubscript{12}O\textsubscript{6} were added into 20 mL of ethyl alcohol at the weight ratio of 1.37: 2.106: 0.613. And then, the solution was milling at 600 rpm for 24 h in a planetary ball mill. And then, the slurry was dried for 12 h in a vacuum oven and heated at 800 °C for 4 h under flowing Ar\textsubscript{2}/H\textsubscript{2} (5%) atmosphere to form the NVP/C.

**Material Characterization**

The crystalline structure and morphology of the products were examined by transmission electron microscope (TEM, JEOL JEM 1011, Japan), high-resolution transmission electron microscopy (HRTEM, JEOL 2100, Japan) and scanning electron microscopy (SEM, JEOL JSM-7100F). The composition and crystalline structure of the synthesized samples were characterized by X-ray diffraction (XRD, Bruker D8 Advanced, Germany). Raman spectra were acquired on a Raman spectrometer (NEXUS 670, Nicolet), and thermal gravimetric analysis (TGA) was
measured on a thermal analyzer (Mettler Toledo TGA/SDTA 851) in the air from room temperature to 800°C. X-ray photoelectron spectroscopy (XPS) measurements were recorded on a Thermo Scientific K-Alpha using an Al Kα X-ray source.

**Electrochemical measurements**

The anode electrode material, MoSe$_2$@C (C-MSC) composites, acetylene black and polyvinylidene fluoride (PVDF) at the proportion of 7:2:1 was adequately milled with the solvent of N-methyl-2-pyrrolidinone (NMP) solution. Then, copper foil was pasted by the forming slurry, dried at 60 °C overnight under vacuum and punched into the round slices (12 mm diameter) with mass loading about 1.0 mg cm$^{-1}$. As the anode electrode in sodium ion battery, the obtained disc was assembled with the counter electrode (fresh sodium foil) and separator (Whatman GF/F) in an argon-filled glove box. Additionally, 1 M NaPF$_6$ in diglyme became the electrolyte transporting ions. Finally, all cyclic voltammetry (CV) curves were measured in a CHI760E electrochemistry workstation at a scan rate of 0.1 mV s$^{-1}$ under the voltage range from 0.01-3.0 V. Galvanostatic discharge/charge tests were carried out on a LAND battery-test instrument (CT2001A) within the potential window of 0.01-3.0 V. Electrochemical impedance spectroscopy (EIS) was tested at a CHI-760E electrochemical workstation in 0.01-100 kHz frequency range.

The homemade Na$_3$V$_2$(PO$_4$)$_3$/C (NVP/C) (80 wt %) as the cathode material in full cell, the acetylene black (10 wt %) and PVDF (10 wt %) were dispersed in NMP solution to form a wilt slurry film adhering to the aluminum foil. After dried at 60 °C under vacuum overnight, the aluminum foil was punched into round slice with the diameter of 16 mm. As the cathode materials, the rate and cycling performance of NVP/C were examined under the potential range of 2.5-3.8 V. With the proportion of capacity for anode MoSe$_2$@C and cathode NVP/C was 1:1.2-1.4 in the full cell, the Galvanostatic measurements were respectively conducted on LAND CT2001A battery test system from 3.8 V to 1.0 V.

**Details of DFT calculations**

We model contact between MoSe$_2$ and Graphene (Gr) by using a 6×4 MoSe$_2$ flake interacting with the Graphene substrate which is a (8×8) periodic layer. All the DFT calculations were conducted with the Vienna Ab initio Simulation Package (VASP). The typical GGA-PBE
functional is used to obtain the total energy, together with DFT-D3 method to count dispersion correction. 3×3×1 k-points were sampled in the calculations. The cutoff energy for the planewave basis is 400 eV and the electronic smearing was chosen as gaussian type with width of 0.03 eV. All the structures are relaxed until the maximum force is smaller than 0.01 eV/Å.
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<tr>
<th>Sample</th>
<th>Capacity/current (considering total weight of composite electrodes)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoSe$_2$@3DOM</td>
<td>382 mAh g$^{-1}$ at 5 A g$^{-1}$ (2000 cycles)</td>
<td>This work</td>
</tr>
<tr>
<td>MoSe$_2$/N,P-rGO</td>
<td>276 mAh g$^{-1}$ at 5 A g$^{-1}$ (1000 cycles)</td>
<td>Adv. Funt. Mater. 2017, 27, 1700522.</td>
</tr>
<tr>
<td>C- MoSe$_2$/rGO</td>
<td>225 mAh g$^{-1}$ at 1 A g$^{-1}$ (1500 cycles)</td>
<td>Nano Res. 2016, 9, 1618.</td>
</tr>
<tr>
<td>MoSe$_2$/HPCFS</td>
<td>234.1 mAh g$^{-1}$ at 1 A g$^{-1}$ (1500 cycles)</td>
<td>Chem. Eng. J. 2018, 233, 2190.</td>
</tr>
<tr>
<td>VG/MoSe$_2$/N-C</td>
<td>298 mAh g$^{-1}$ at 2 A g$^{-1}$ (1000 cycles)</td>
<td>Adv. Energy. Mater. 2017, 7, 1061804.</td>
</tr>
<tr>
<td>MoSe$_2$/G</td>
<td>368 mAh g$^{-1}$ at 3.2 A g$^{-1}$ (1500 cycles)</td>
<td>Nano Energy, 2018, 47, 224.</td>
</tr>
<tr>
<td>MoSe$_2$ nanotube</td>
<td>228 mAh g$^{-1}$ at 1 A g$^{-1}$ (1500 cycles)</td>
<td>J. Mater. Chem. A 2017, 5, 24859.</td>
</tr>
<tr>
<td>MoSe$_2$/P-C@TiO$_2$</td>
<td>214 mAh g$^{-1}$ at 5 A g$^{-1}$ (8000 cycles)</td>
<td>Adv. Sci. 2019, 6,1081222.</td>
</tr>
<tr>
<td>MoSe$_2$@CoSe/N-C</td>
<td>347 mAh g$^{-1}$ at 2 A g$^{-1}$ (300 cycles)</td>
<td>Energy Storage Mater. 2018, 21, 97.</td>
</tr>
<tr>
<td>MoSe$_2$-rGO-CNT</td>
<td>335 mAh g$^{-1}$ at 1 A g$^{-1}$ (400 cycles)</td>
<td>ACS Appl. Mater. Inter. 2017, 9, 10673.</td>
</tr>
<tr>
<td>Mo(Se$<em>{0.85}$S$</em>{0.15}$)$_2$</td>
<td>312 mAh g$^{-1}$ at 1A g$^{-1}$ (100 cycles)</td>
<td>Small 2015, 11, 5667.</td>
</tr>
<tr>
<td>O- MoSe$_2$/SnO$_2$</td>
<td>298 mAh g$^{-1}$ at 1 A g$^{-1}$ (100 cycles)</td>
<td>Chem. Eng. J. 2018, 354, 1164.</td>
</tr>
</tbody>
</table>