Hierarchical MoS$_2$ Hollow Architectures with Abundant Mo Vacancies for Efficient Sodium Storage

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Figure S1. FESEM (a and b), TEM (c) images and XRD pattern (d) of HZIF-Zn/Mo. FESEM images clearly demonstrate the HZIF-Zn/Mo has a uniformly microcube morphology with smooth surface over the whole particle (Figures S1a and S1b). The corresponding transmission electron microscopy (TEM) characterization (Figure S1c) verifies the solid nature. The XRD pattern of HZIF-Zn/Mo was recorded at room temperature. The peak positions of simulated and experimental patterns are in good agreement with each other, indicating the phase purity of the as-synthesized samples (Figure S1d).
**Figure S2.** FESEM (a, and b) and TEM (c) images of HMF-MoO$_x$/ZnS. FESEM characterization shows that the obtained HMF-MoO$_x$/ZnS well inherits the microcube shape but displays a rough surface composed of numerous nanoparticles, indicating the *in situ* topotactic transformation of HZIF-Zn/Mo in TAA solution (Figures 2b, 2c, S2a, and S2b). From the cracked particle shown in the Figure 2c, the formation of a hollow structure can be discerned directly. The hollow interior of the HMF-MoO$_x$/ZnS is also unambiguously elucidated by the sharp contrast between the solid shell and the inner cavity under TEM observations (Figure S2c).
Figure S3. FESEM (a and b), TEM (c) images and XRD pattern (d) of HZIF-Zn/Mo after 2h of solvothermal sulfidation. Schematic illustration of the synthesis procedure for HMF-MoO₃/ZnS hollow structure (e). Time-dependent experiments were carried out to monitor the formation process of the hollow structure. By adjusting the reaction time with TAA to 2h, XRD analysis indicates the coexistence of residual HZIF-Zn/Mo cores and crystallographic ZnS shell (Figure S3d). The HZIF-Zn/Mo core can be discerned unambiguously from the cracked particles (Figure S3b). TEM further confirms the formation of core-shell structure (Figure S3c). The evolution of the hollow interior in this system is different with previous reports. Specifically, at the initial solvothermal sulfidation stage, the strong reductive S²⁻ ions released from TAA
upon hydrolyzation quickly react with the Zn\(^{2+}\) ions to form a thin layer of crystallographic ZnS in the near-surface region of HZIF-Zn/Mo. Therefore, the ultrathin ZnS shell is formed around the scaffold of each HZIF-Zn/Mo microcubes, which acts as a physical barrier to prevent the direct contact and chemical reaction between outside S\(^{2-}\) ions and inner metal ions. As the reaction proceeds, the different diffusion rates through the newly formed ZnS shell of the inward diffusion of S\(^{2-}\) ions and the outward flow Zn\(^{2+}\) ions and MoO\(_x\) components is the key to form the hollowing structure. The Zn\(^{2+}\) ions with the smaller ionic radium (74 pm) are much easier to penetrate the formed ZnS shell to react with S\(^{2-}\) (184 pm) on the outer surface, while at the same time, more MoO\(_x\) components coupled with bits of organic ligands, gathered in the internal surface of the ZnS shell owing to high diffusion resistance, which finally results in the formation of the hybrid shell of MoO\(_x\)/ZnS. Therefore, the consecutive outward flow of Zn\(^{2+}\) ions and/or MoO\(_x\) components will consume the inner organic framework, causing a hollow void inside the hybrids.

Figure S4. FESEM images of HMF-MoS\(_2\).
Figure S5. TEM image (a) and EDX spectrum (b) of HMF-MoOₓ/ZnS.
Figure S6. TEM images of HMF-MoS$_2$. 
Figure S7. FESEM (a and b) and TEM (c and d) images of pristine MoS$_2$. 
Figure S8. Schematic illustration of the molybdenum defects in HMF-MoS$_2$ (a) and HRTEM images of HMF-MoS$_2$ (b). The numerous small pits denoted by the red dashed line illustrate the formation of defects on HMF-MoS$_2$. 
Figure S9. Raman spectrum of HMF-MoS$_2$ and pristine MoS$_2$. 

- $E'_{2g}/A_{1g} = 0.47$
- $E'_{3g}/A_{1g} = 0.39$
**Figure S10.** XPS spectra: survey spectrum of HMF-MoS₂ (a), high-resolution Mo 3d XPS spectra of HZIF-Zn/Mo, HMF-MoOₓ/ZnS, and HMF-MoS₂ (b), high-resolution S 2p XPS spectra of HMF-MoOₓ/ZnS and HMF-MoS₂ (c) and high-resolution C 1s XPS spectra of HMF-MoS₂ (d). The high-resolution Mo 3d XPS spectrum of HMF-MoS₂ in Figure S10b shows a weak peak of S 2s at 226.6 eV and two strong peaks at 229.4 and 232.5 eV, which are corresponding to the Mo 3d⁵/₂ and Mo 3d³/₂ of Mo⁴⁺ of MoS₂. For HZIF-Zn/Mo, only peaks corresponding to the Mo⁶⁺ 3d³/₂ and Mo⁶⁺ 3d⁵/₂ at 235.06 and 231.96 eV, respectively, have been observed. With the reaction with thioacetamide (TAA), a new strong peak related to the S 2s at 225.71 eV has been observed for HMF-MoOₓ/ZnS. This result is consistent with the S-Zn bonded structure located at a low chemical bonding state of 161.2 and 162.4 eV in S 2p spectrum (Figure S10c). The S 2p XPS spectrum in HMF-MoS₂ shows two strong peaks at 162.2 and 163.4 eV, which are attributed to the S 2p₃/₂ and S 2p₁/₂ binding energy for S²⁻ of MoS₂.
Figure S11. TGA curve of HMF-MoS$_2$. The initial mass loss of ≈1% below 200 °C is mainly due to the evaporation of surface adsorbed moisture. Given the fact that the carbon is burnt out and the MoS$_2$ is totally converted into MoO$_3$ with 82.1 wt. % of original mass retained. Based on the following chemical reaction (1), the contents of the MoS$_2$ and carbon are calculated to be ≈92 wt. % and ≈8 wt. %, respectively.

$$2\text{MoS}_2 (s) + 7\text{O}_2 = \text{MoO}_3 + 4\text{SO}_2$$  \hspace{0.5cm} (1)
**Figure S12.** \( \text{N}_2 \) sorption isotherms at 77 K of pristine MoS\(_2\) and HMF-MoS\(_2\) (a) and the corresponding pore size distributions and cumulative pore volume curve (b) for HMF-MoS\(_2\) based on the density functional theory (DFT) method.
Figure S13. Cathodic peak currents of HMF-MoS$_2$ at various scan rates of 0.1-0.8 mV s$^{-1}$. 
Figure S14. The proposed crystal structure of the MoS$_2$ with Mo vacancies (a). The charge density distribution of pristine MoS$_2$ (b).
Figure S15. I-V curves of the pressed pellet of HMF-MoS$_2$ and pristine MoS$_2$. The conductivity of the HMF-MoS$_2$ and pristine MoS$_2$ powder pellets was measured with a two-probe method using Keithley 4200. The pellets were pressed at a pressure of ≈1 GPa. The powder pellets were connected to the system by gold wires with both surfaces of the pellets covered by silver paste.
# Table S1 Summary of discharge of various MoS₂-based anodes.

<table>
<thead>
<tr>
<th>MoS₂-based anodes</th>
<th>discharge capacity (mAh g⁻¹)</th>
<th>Voltage range (V)</th>
<th>Current (mA g⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMF-MoS₂</td>
<td>384 (after 100 cycles)</td>
<td>0.01-3</td>
<td>100</td>
<td>Present study</td>
</tr>
<tr>
<td>1T MoS₂</td>
<td>313 (after 200 cycles)</td>
<td>0.01-3</td>
<td>50</td>
<td>Adv. Funct. Mater. 2017, 1702998</td>
</tr>
<tr>
<td>E-MoS₂/SG/carbon fibers</td>
<td>241 (after 700 cycles)</td>
<td>0.01-3</td>
<td>1000</td>
<td>Nano energy 2017, 41, 66-74</td>
</tr>
<tr>
<td>MoS₂/SG</td>
<td>437 (after 100 cycles)</td>
<td>0.005-3</td>
<td>100</td>
<td>Adv. Funct. Mater. 2017, 1702562.</td>
</tr>
<tr>
<td>CC@CN@MoS₂</td>
<td>619.2 (after 100 cycles)</td>
<td>0.01-3</td>
<td>200</td>
<td>Adv. Funct. Mater. 2017, 27, 1702116.</td>
</tr>
<tr>
<td>m-C/MoS₂ hollow nanosphere</td>
<td>320 (after 550 cycles)</td>
<td>0.01-3</td>
<td>1000</td>
<td>Nano energy 2018, 51, 546-555</td>
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<tr>
<td>(MoS₂/CF)@MoS₂@C</td>
<td>332.6 (after 1000 cycles)</td>
<td>0.01-2.5</td>
<td>1000</td>
<td>Energy Storage Materials 2018, 15, 22-30.</td>
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</tbody>
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