Supporting Information

Bi$_2$MoO$_6$ Microsphere with Double-polyaniline Layers towards Ultra-stable Lithium Energy Storage by Reinforced Structure

Yang Zhang, Ganggang Zhao, Peng Ge, Tianjing Wu, Lin Li, Peng Cai, Cheng Liu, Guoqiang Zou*, Hongshuai Hou, Xiaobo Ji

College of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, China.

*Corresponding author: Guoqiang Zou

*E-mail: gq-zou@csu.edu.cn
1. EXPERIMENTAL SECTION

1.1. Preparation of Bi$_2$MoO$_6$ microspheres

The raw Bi$_2$MoO$_6$ was prepared by a hydrothermal method. Firstly, 6 mmol Bi(NO)$_3$·5H$_2$O and 3 mmol Na$_2$MoO$_4$ were separately dissolved in 30 mL ethylene glycol, and then stirring for about 10 min, respectively. Secondly, the Na$_2$MoO$_4$ solution was added into Bi(NO)$_3$·5H$_2$O solution under magnetic stirring, then 60 mL of absolute ethanol was added into the mixed solution and 4 g polyvinyl pyrrolidone (PVP), as the surfactant, was also added. After stirring for about 40 min, the above solution was transferred into Teflon-lined stainless steel autoclave and heated at 150°C for 8 h. Next, the yellow precursor was collected, washed several times with distilled water, and dried at 60°C for 12 h under vacuum. Finally, sintering the precursor in nitrogen at 500°C for 2 h with heating rate of 5°C min$^{-1}$ to get the high crystallinity Bi$_2$MoO$_6$.

1.2. Preparation of Bi$_2$MoO$_6$@PANI

The Bi$_2$MoO$_6$@PANI was prepared by chemical oxidative polymerization of aniline on the surfaces of Bi$_2$MoO$_6$ particles. Firstly, 0.4 g Bi$_2$MoO$_6$ was dissolved in 200 mL distilled water and then sonicated for about 40 min. At the same time, 90 µL aniline and 0.0375 g tartaric acid were dissolved in 10 mL distilled water and stirring for 0.5 h, then added into the Bi$_2$MoO$_6$ solution under magnetic stirring and kept 0-5°C for 0.5 h. Next, 10 mL of oxidant aqueous solution containing 0.228 g ammonium persulfate, which had been cooled in advance in an ice-water bath, was poured into the mixture solution. After the polymerization reaction at 0-5°C for 6 h,
the as-prepared samples were washed several times with deionized water and ethanol, assisted by centrifugation, and then dried at 60°C for 12 h under vacuum. Finally, calcining the solid product in nitrogen at 400°C for 2 h with heating rate of 5°C min\(^{-1}\) to get the target product Bi\(_2\)MoO\(_6\)@PANI.

1.3. Material characterization

To investigate the compositions, crystal structural feature and chemical valence states, XRD (Rigaku Ultima IV, 18 kW, Cu K\(_\alpha\) radiation), Raman (Jobin-Yvon Lab RAM HR-800) and Fourier transform infrared (FT-IR, AVTA-TAR, 370), XPS (Thermo Scientific Escalab, 250xi, US) were employed. The thermal evolution of the sample was carried out using TG analysis (TGA, STA 2500 Regulus). The morphologies were revealed by the Field-emission scanning electron microscopy (FESEM) (FEI Quanta 200) and Transmission electron microscopy (TEM) (JEM-2100F).

1.4. Electrochemical measurements

The electrochemical performances of the target materials were investigated through the coin-type 2016 cells which were assembled in argon filled glove box. The electrode can be assembled by following steps: First, mixing as-prepared samples, binder carboxymethyl cellulose (CMC) and conductive additives (Super P) (70:15:15). After the slurry was mixed well enough then painted it on a copper foil and dried overnight under vacuum. Next, the prepared active materials were punched to some circular pieces with the mass loading around of 1.0-1.3 mg/cm\(^2\) and applied in half-cells as work electrode, while the lithium tablets as the counter electrode, the
polypropylene film (Celgard 2400) as separator and the electrolyte, which was made up of 1 M LiPF$_6$ in ethylene carbonate (EC) and diethyl carbonate (DC) (1:1 by volume) solution. Arbin battery cycler (BT2000, USA) was applied to conduct the galvanostatic cycling and rate performances. The cyclic voltammetry (CV) measurements and electrochemical impedance spectroscopy (EIS) were investigated using Autolab (MULTI AUTOLAB M204) electrochemical workstation.
Figure S1 XPS spectra of (a) Bi 4f, (b) Mo 3d, (c) O 1s of pure Bi₂MoO₆
Figure S2 SEM spectra of (a-b) pure Bi$_2$MoO$_6$, (c-d) Bi$_2$MoO$_6$@PANI. After the introduction of conductive polyaniline, the inner and outer surfaces of Bi$_2$MoO$_6$ became smoother, the nanosheets cannot be observed anymore, revealing that the polyaniline were successfully coated in the dual surfaces.
Figure S3 XRD pattern of Bi$_2$MoO$_6$ precursor without calcining
Figure S4 Raman spectra of pure Bi$_2$MoO$_6$ after 1st cycles
Figure S5 CV curves of Bi$_2$MoO$_6$ and Bi$_2$MoO$_6$@PANI at 2.0, 5.0, 8.0 and 10 mV s$^{-1}$
Figure S6 The linear relation $i/v^{1/2}-v^{1/2}$ of Bi$_2$MoO$_6$@PANI at various potential;
Preparation of Bi$_2$MoO$_6$ nanoparticles

The preparation of Bi$_2$MoO$_6$ nanoparticles was basically identical to that of the Bi$_2$MoO$_6$ microspheres except the heated time was replaced with 16h.

Figure S7 (a) XRD pattern; (b) the cycling performance at 100 mA g$^{-1}$; (c-d) SEM images of Bi$_2$MoO$_6$ nanoparticles
Figure S8 The linear relation between $\omega^{1/2}$ and $Z''$ at various cycles of Bi$_2$MoO$_6$. 
Figure S9 CV curves at 0.2 mV s⁻¹ after 200th cycles
Figure S10 Nyquist plots of Bi$_2$MoO$_6$ at (a) discharged conditions, (b) charged conditions and (c) the corresponding linear relation of $\omega^{1/2}$ versus $-Z''$. 
Fig. S11 The corresponding linear relation of $\omega^{1/2}$ versus $-Z''$ of Bi$_2$MoO$_6$@PANI at different potentials.
Figure S12 The lithium ions diffusion coefficients of Bi$_2$MoO$_6$ and Bi$_2$MoO$_6$@PANI at different voltages
Table S1 The corresponding resistance parameters of samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>$R_e$</th>
<th>$R_f$</th>
<th>$R_{ct}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$MoO$_6$</td>
<td>3.106</td>
<td>446</td>
<td>34.15</td>
</tr>
<tr>
<td>Bi$_2$MoO$_6$@PANI</td>
<td>3.735</td>
<td>339.9</td>
<td>16.5</td>
</tr>
</tbody>
</table>
Table S2 The lithium ion diffusion coefficients ($D_{Li^+}$) of samples at various cycles

<table>
<thead>
<tr>
<th>Cycles</th>
<th>Bi$_2$MoO$_6$</th>
<th>Bi$_2$MoO$_6$@PANI</th>
</tr>
</thead>
<tbody>
<tr>
<td>20$^{th}$</td>
<td>4.31</td>
<td>5.64</td>
</tr>
<tr>
<td>50$^{th}$</td>
<td>1.52</td>
<td>3.31</td>
</tr>
<tr>
<td>80$^{th}$</td>
<td>1.31</td>
<td>1.61</td>
</tr>
<tr>
<td>100$^{th}$</td>
<td>1.13</td>
<td>1.93</td>
</tr>
<tr>
<td>120$^{th}$</td>
<td>1.00</td>
<td>1.74</td>
</tr>
<tr>
<td>150$^{th}$</td>
<td>1.10</td>
<td>1.73</td>
</tr>
<tr>
<td>200$^{th}$</td>
<td>0.94</td>
<td>1.54</td>
</tr>
</tbody>
</table>