Supporting Information

MOF derived ZnCo$_2$O$_4$ porous hollow spheres functionalized with Ag nanoparticles for a long-cycle and high-capacity lithium ion battery anode

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**Fig. S1** TG and DTG curves of BM-ZIF_PS in the temperature range of 50–750 °C under air atmosphere.
Fig. S2 (a) SEM image of ZnCo$_2$O$_4$ HSs, (b) STEM image of ZnCo$_2$O$_4$@Ag HSs, and (c) SAED patterns of ZnCo$_2$O$_4$@Ag HSs.
Fig. S3 TEM analyses of ZnCo$_2$O$_4$@Ag HSs \textit{via} Ag-mirror reaction using 1.7 mM (a-d) and 15 mM (e-h) of AgNO$_3$. TEM images (a,e), high magnification TEM images (b,f), STEM images (c,g), and EDS elemental mapping images (d,h).
Fig. S4 SEM images of (a) BM-ZIFs and (b) ZnCo$_2$O$_4$ NPs after calcination at 450 °C, and (c) XRD analysis of ZnCo$_2$O$_4$ NPs.
Fig. S5 CV curves of 1st, 2nd, and 5th cycles at a scan rate of 0.1 mV s\(^{-1}\) for (a) ZnCo\(_2\)O\(_4\) NPs, (b) ZnCo\(_2\)O\(_4\) HSs, and (c) ZnCo\(_2\)O\(_4\)@Ag HSs, respectively, with a voltage range of 0.01-3.0 V. CV curves of 1st, 2nd, and 5th cycles at a scan rate of 5.0 mV s\(^{-1}\) for (d) ZnCo\(_2\)O\(_4\) NPs, (e) ZnCo\(_2\)O\(_4\) HSs, and (f) ZnCo\(_2\)O\(_4\)@Ag HSs.
Fig. S6 High-resolution XPS analysis spectrum of Ag 3$d$ for ZnCo$_2$O$_4$@Ag HSs after 10 times of galvanostatic charging/discharging (a) with fully lithiated state, and (b) fully delithiated state.
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**Fig. S8** SEM images of the surface of (a) ZnCo$_2$O$_4$ NPs, (b) ZnCo$_2$O$_4$ HSs, and (c) ZnCo$_2$O$_4$@Ag HSs electrodes before cycling. *Ex-situ* SEM images of fully delithiated (d) ZnCo$_2$O$_4$ NPs, (e) ZnCo$_2$O$_4$ HSs, and (f) ZnCo$_2$O$_4$@Ag HSs electrodes after 200 cycles.
Fig. S9 Equivalent circuit model for ZnCo$_2$O$_4$ NPs, ZnCo$_2$O$_4$ HSs, and ZnCo$_2$O$_4$@Ag HSs electrodes after cycling.
**Fig. S10** Nyquist plots of the fully delithiated ZnCo$_2$O$_4$ NPs, ZnCo$_2$O$_4$ HSs, and ZnCo$_2$O$_4$@Ag HSs before cycling.
Table S1. Capacity values of ZnCo$_2$O$_4$ NPs, ZnCo$_2$O$_4$ HSs, and ZnCo$_2$O$_4$@Ag HSs at high current densities of 10 A g$^{-1}$, 15 A g$^{-1}$, 20 A g$^{-1}$, and 0.5 A g$^{-1}$.

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<th>10 A g$^{-1}$</th>
<th>15 A g$^{-1}$</th>
<th>20 A g$^{-1}$</th>
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<tr>
<td>ZnCo$_2$O$_4$ NPs</td>
<td>562 mAh g$^{-1}$</td>
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<td>ZnCo$_2$O$_4$ HSs</td>
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<td>479 mAh g$^{-1}$</td>
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<td>ZnCo$_2$O$_4$@Ag HSs</td>
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<td>Active material</td>
<td>Cycling performance</td>
<td>Rate capability</td>
<td>Reference</td>
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<tr>
<td>Mesoporous ZnCo$_2$O$_4$ microspheres</td>
<td>721 mAh g$^{-1}$ after 80 cycles</td>
<td>382 mAh g$^{-1}$ at 5.0 A g$^{-1}$</td>
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<td>Porous spinel Zn$<em>x$Co$</em>{3-x}$O$_4$ hollow polyhedra</td>
<td>990 mAh g$^{-1}$ after 50 cycles at 0.1 A g$^{-1}$</td>
<td>575 mAh g$^{-1}$ at 9.0 A g$^{-1}$</td>
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<td>ZnO/ZnCo$_2$O$_4$/C core/shell</td>
<td>669 mAh g$^{-1}$ after 250 cycles at 0.5 A g$^{-1}$</td>
<td>715 mAh g$^{-1}$ at 1.6 A g$^{-1}$</td>
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<td>Te@ZnCo$_2$O$_4$ nanofibers</td>
<td>956 mAh g$^{-1}$ after 100 cycles at 0.1 A g$^{-1}$</td>
<td>587 mAh g$^{-1}$ at 1.0 A g$^{-1}$</td>
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<td>ZnCo$_2$O$_4$ 3D hierarchical twin microspheres</td>
<td>550 mAh g$^{-1}$ after 2000 cycles at 5.0 A g$^{-1}$</td>
<td>790 mAh g$^{-1}$ at 10 A g$^{-1}$</td>
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<td>ZnCoO$_4$@Ag HSs</td>
<td>616 mAh g$^{-1}$ after 900 cycles at 1.0 A g$^{-1}$</td>
<td>572 mAh g$^{-1}$ at 20 A g$^{-1}$</td>
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Table S2. Cycling performance and rate capabilities of representative ZnCo$_2$O$_4$ anode materials for Li-ion batteries.
Table S3. Fitted electrochemical impedance component values of ZnCo$_2$O$_4$ NPs, ZnCo$_2$O$_4$ HSs, and ZnCo$_2$O$_4$@Ag HSs electrodes after (a) 1 cycle and (b) 200 cycles.

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<th>$R_{SEI}$ (Ω)</th>
<th>$R_{CT}$ (Ω)</th>
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<td>ZnCo$_2$O$_4$ NPs</td>
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<td>ZnCo$_2$O$_4$ HSs</td>
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<td>19.6</td>
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<td>ZnCo$_2$O$_4$@Ag HSs</td>
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<th>$R_{SEI}$ (Ω)</th>
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<td>ZnCo$_2$O$_4$ NPs</td>
<td>4.58</td>
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<td>ZnCo$_2$O$_4$ HSs</td>
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<td>ZnCo$_2$O$_4$@Ag HSs</td>
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References


