Supporting Information

Coaxial Zn$_2$GeO$_4$@Carbon Nanowires Directly Grown on Cu Foils as High-Performance Anodes for Lithium Ion Batteries

Weimin Chen, Liyou Lu, Scott Maloney, Ying Yang, and Wenyong Wang*

Department of Physics and Astronomy, University of Wyoming, Laramie, WY 82071, USA

*E-mail: wwang5@uwyo.edu
Experimental method

Synthesis of h-Zn$_2$GeO$_4$ and h-Zn$_2$GeO$_4$@C. h-Zn$_2$GeO$_4$ nanowires were synthesized by a hydrothermal reaction. GeO$_2$ (10 mmol) and Zn(CH$_3$COO)$_2$·2H$_2$O (10 mmol) were mixed in a solvent including 20 mL ethylenediamine and 10 mL deionized H$_2$O, and the mixture was kept in the oven at 180 °C for 24 h. Carbon coating on the h-Zn$_2$GeO$_4$ nanowires was created by immersing them in a 0.5 M aqueous glucose solution for 24 h, followed by sintering the h-Zn$_2$GeO$_4$-glucose samples at 500 °C in Ar gas for 2 h. The working electrode of h-Zn$_2$GeO$_4$ or h-Zn$_2$GeO$_4$@C was prepared using pre-fabricated h-Zn$_2$GeO$_4$ or h-Zn$_2$GeO$_4$@C nanowires with super P and polyvinylidene difluoride with a weight ratio of 8:1:1.

Figure S1. TGA curve of typical Zn$_2$GeO$_4$@C nanowires. The Zn$_2$GeO$_4$ content of nanowires estimated from the TGA is 86.9 %. The TGA data was collected in air with a heating rate of 10 °C min$^{-1}$. 
Figure S2. (a) Dark-field TEM image of the Zn$_2$GeO$_4$@C nanowire. (b) EDX line-scan element distributions of C, Zn, Ge and O along the line shown in (a).

Figure S3. (a, b) SEM images of the ZGO@C nanowires. (c) Cross-sectional SEM image of ZGO@C nanowires on Cu foil. The nanowires showed arbitrary growth directions.
Figure S4. An EDX spectrum of a typical coaxial Zn$_2$GeO$_4@C$ nanowire, which demonstrates the presence of Zn, Ge, O, and C in the structure. The Cu signals are from the Cu foil substrate.

Figure S5. Cyclic performance of 1 h and 3 h ZGO@C/Cu electrodes at 0.2 A g$^{-1}$. After 50 cycles, the capacity of 1 h ZGO@C/Cu electrode decays quickly to 596 mAh g$^{-1}$, while the 3 h ZGO@C/Cu electrode is relatively stable and exhibits a capacity of 811 mAh g$^{-1}$ after 50 cycles.
Figure S6. (a) SEM image of the ZGO@C/Cu electrode after 50-cycle test at 0.2 A g\textsuperscript{-1}. (b) SEM image of the ZGO@C/Cu electrode after 100-cycle test at 2.0 A g\textsuperscript{-1}. The images show that a SEI layer is formed on the surface of the Zn\textsubscript{2}GeO\textsubscript{4}@carbon nanowires.
Figure S7. TEM image of h-Zn$_2$GeO$_4$ nanowires.

Figure S8. XRD spectra of h-Zn$_2$GeO$_4$ and h-Zn$_2$GeO$_4$@C nanowires. Both patterns fit well to the characteristic peaks of crystalline Zn$_2$GeO$_4$ (JCPDS card No. 11-0687).
Table S1: Comparison of electrochemical performance of Zn$_2$GeO$_4$-based or Zn-based ternary metal oxide LIB anodes

<table>
<thead>
<tr>
<th>Materials</th>
<th>Low Current density (A g$^{-1}$)</th>
<th>Reversible Capacity (mAh g$^{-1}$)</th>
<th>High Current density (A g$^{-1}$)</th>
<th>Reversible Capacity (mAh g$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$_2$GeO$_4$ nanorods</td>
<td>0.4</td>
<td>615</td>
<td>4.0</td>
<td>510</td>
<td>2</td>
</tr>
<tr>
<td>Zn$_2$GeO$_4$/N-doped graphene nanocomposites</td>
<td>0.1</td>
<td>1044</td>
<td>3.2</td>
<td>321</td>
<td>3</td>
</tr>
<tr>
<td>Zn$_2$GeO$_4$ nanoparticles</td>
<td>0.4</td>
<td>1250</td>
<td>6.4</td>
<td>470</td>
<td>4</td>
</tr>
<tr>
<td>Zn$_2$GeO$_4$/graphene oxide nanocomposites</td>
<td>0.2</td>
<td>1155</td>
<td>3.2</td>
<td>522</td>
<td>5</td>
</tr>
<tr>
<td>Zn$_2$GeO$_4$ nanorod/graphene composites</td>
<td>0.2</td>
<td>768</td>
<td>0.8</td>
<td>780</td>
<td>6</td>
</tr>
<tr>
<td>ZnxCo$_{3-x}$O$_4$ hollow polyhedra</td>
<td>0.1</td>
<td>990</td>
<td>9.0</td>
<td>575</td>
<td>7</td>
</tr>
<tr>
<td>ZnMn$_2$O$_4$/graphene nanosheets</td>
<td>0.5</td>
<td>800</td>
<td>3.2</td>
<td>568</td>
<td>8</td>
</tr>
<tr>
<td>Coaxial Zn$_2$GeO$_4$@carbon nanowires</td>
<td>0.2</td>
<td>1112</td>
<td>10.0</td>
<td>440</td>
<td>This work</td>
</tr>
</tbody>
</table>

Compared with previously published results of Zn$_2$GeO$_4$-based or Zn-based ternary metal oxide anodes, the ZGO@C/Cu electrode synthesized in this work exhibits higher capacity and stability at high-rate cycling.

References


