Electronic Supplementary Information (ESI)

**Graphene boosted Cu$_2$GeS$_3$ for advanced lithium-ion battery**

Lin Fu, a,b‡ Chuanjian Zhang, a‡ Bingbing Chen, a Zhonghua zhang, a,b Xiaogang Wang, a,* Jingwen Zhao, a Jianjiang He, a,b Huiping Du, a,b and Guanglei Cui a,*

a Qingdao Industrial Energy Storage Research Institute, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, No.189 Songling Road, Laoshan District, Qingdao, 266101, China.
b University of Chinese Academy of Sciences, No.19 Yuquan Road, Shijingshan District, Beijing, 100190, China.
‡ These authors contributed equally to this work.
E-mail: wangxg@qibebt.ac.cn; cuigl@qibebt.ac.cn.

Fig. S1 Schematic diagram for the preparation process of CGSN and CGS@RGO, respectively.
Fig. S2 XRD pattern of the CuGeO$_3$.

Fig. S3 (a) Raman spectra of GO, RGO and CGS@RGO. (b) TGA curve of the CGS@RGO.

Fig. S3b shows the TGA curve of CGS@RGO and similar phenomenon was reported in the previous study of graphene–metal sulfide composites.$^1$ The weight loss rate of graphene content is calculated based on the Cu$_2$GeS$_3$ and graphene and the residual products only include CuO and GeO$_2$.

Fig. S4 (a) SEM and (b) TEM images of the RGO.
Fig. S5 High-resolution XPS spectra of O 1S in the CGS@RGO composite.

Fig. S6 (a) SEM and (b) TEM images of CuGeO$_3$. (c) The cross-sectional images and (d) digital photograph of CGS@RGO.
Fig. S7 (a) Cyclic voltammetry of the CGS@RGO at a scanning rate of 0.2 mV s$^{-1}$. (b) The cycling performance and (c) the initial two charge and discharge curves of the RGO electrode at a current density of 1000 mA g$^{-1}$. (d) The cycling performance of the CuGeO$_3$ electrode at a current density of 1000 mA g$^{-1}$.

The RGO was prepared by direct annealing GO with sublimed sulfur in argon atmosphere at 500 °C for 4 h. The RGO of CGS@RGO only offers a low capacity (about 50 mAh g$^{-1}$ based on 13.5% RGO in the CGS@RGO) at a current density of 1000 mA g$^{-1}$ as shown in Fig. S7b.

Fig. S8. SEM images of the CGSN electrode (a) before cycling and (b) after 10 charge/discharge cycles. (c, d) SEM images of the CGS@RGO electrode after 10 charge/discharge cycles.
Table S1. Comparison of CGS@RGO electrodes with those in previously published Cu-Ge-based anodes of LIBs.

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>Current density</th>
<th>Charge specific capacity (mA h g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1st</td>
</tr>
<tr>
<td>CGS@RGO (this work)</td>
<td>1000 mA g(^{-1})</td>
<td>853.1</td>
</tr>
<tr>
<td>CuGeO(_2)</td>
<td>150 mA g(^{-1})</td>
<td>927</td>
</tr>
<tr>
<td>CuGeO(_3)-graphene(^3)</td>
<td>200 mA g(^{-1})</td>
<td>1265</td>
</tr>
<tr>
<td></td>
<td>400 mA g(^{-1})</td>
<td>~1050</td>
</tr>
<tr>
<td>Cu(_3)Ge/GeO(_2)/CuGeO(_3)</td>
<td>200 mA g(^{-1})</td>
<td>971</td>
</tr>
<tr>
<td>Cu(_3)Ge/Ge@graphene(^5)</td>
<td>1C</td>
<td>N/A</td>
</tr>
<tr>
<td>Cu(_3)Ge/C(^6)</td>
<td>150 mA g(^{-1})</td>
<td>~1005</td>
</tr>
<tr>
<td>Cu(_3)Ge/Ge/C(^7)</td>
<td>0.5C</td>
<td>1352</td>
</tr>
<tr>
<td>GeO(_2)/Cu/C(^8)</td>
<td>0.2C</td>
<td>869</td>
</tr>
</tbody>
</table>

In the table S1, the capacity of Cu\(_3\)Ge/Ge/C (ref. 7) is based on active Ge content in the Cu\(_3\)Ge/Ge/C composites, which does not include the Ge present in the Cu\(_3\)Ge content.\(^7\)

Fig. S9 EIS curves of the CGS@RGO and CGSN electrode before cycling and the inset equivalent circuit to fit the EIS. The Rs, Rct, C and Zw denote the internal resistance, charge transfer resistance, double-capacitance resistance and Warburg impedance of lithium ion diffusion, respectively.
It is known that the diffusion coefficient ($D$) is obtained as the MSD over time:

$$D = \frac{1}{6t} \sum_i \langle [\mathbf{r}_i(t + t_0)]^2 - [\mathbf{r}_i(t_0)]^2 \rangle$$

Where $\mathbf{r}_i(t)$ is the displacement of the $i$-th lithium ion at the time, and $\langle \rangle$ represents an average over the ensemble of atoms. It is evident from Fig. S10a, the diffusion coefficient of Li atoms is much more quickly in the CGS than that of CuGeO$_3$ and GeS$_2$. Structural relaxation of CGS were performed with generalized gradient approximation (GGA) in the projector augmented wave (PAW) method exchange-correlation functional, as implemented in the Vienna Ab initio Simulation Package (VASP). The plane-wave basis set was determined with a cutoff energy of 500 eV and the K-point mesh was defined such that the spacing of k-points became less than 0.25 Å for all calculations. The crystal structure optimized was shown in Fig.S10b. It was found that the the lattice of CGS was $a = 6.519$, $b = 11.419$ and $c = 6.458$ with Cc space group, consisting with the experimental results. What’s more, to elucidate the lithium ions diffusivity mechanism, the Ab initio Molecular Dynamic Simulations (AIMD) methods were performed. A final energy optimized was used to ensure the modeling in a local energy minimum, which was modeled by attaching an amorphous lithium atom layer of 24 atoms to the surface of a $1 \times 1 \times 2$ CGS supercell (49 atoms). Simulations were carried out using the NVT ensemble with the temperature controlled With a Nose thermostat at 700K for this modeling. Fig. S10c shows the structure evolution of the diffusion Li ions upon annealing at 700 K for 3 ps.
References


