Supporting Information

**Design of Coherent Anode Materials with 0D Ni₃S₂ Nanoparticles Self-assembled on 3D Interconnected Carbon Networks for Fast and Reversible Sodium Storage**

Xu Zhao, a,b,c Hong-En Wang, c Robert C. Massé, c Jian Cao, a Jiehe Sui, a,b Jiangyu Li, d Wei Cai, b,* and Guozhong Cao c,*

a State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin 150001, China.
b School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China.
c Department of Materials Science and Engineering, University of Washington, Seattle, WA 98195, USA.
d Department of Mechanical Engineering, University of Washington, Seattle, WA 98195, USA.

Corresponding author: weicai@hit.edu.cn; gzcao@u.washington.edu

Figure S1. Optical photograph and corresponding SEM images of different periods in preparing coherent Ni₃S₂/C nanocomposites: (a) Ni(NO₃)₂ · 6H₂O + citric acid + thiourea adsorbed NaCl after freeze-drying, SEM demonstrating a uniform attaching of Ni(NO₃)₂ · 6H₂O + citric acid + thiourea precursors onto NaCl cubic surface; (b) Ni₃S₂/C adsorbed NaCl after annealing in N₂ (800 °C in N₂ for 2h, ramping rate was 5 °C/min), SEM indicating as-prepared Ni₃S₂/C coated on the cubic surface of NaCl template homogeneously; (c) coherent Ni₃S₂/C hybrids after NaCl removal, which has a low density to float on water, SEM images show an overall porous interconnected nanostructure.
Figure S2. XRD patterns of coherent Ni$_3$S$_2$/C nanocomposite (a) before and (b) after washing to dissolve NaCl templates, in addition to strong peaks of cubic phase NaCl (JCPDS No. 87-0712), other peaks are in good accordance with Ni$_3$S$_2$ of Heazlewoodite phase (JSPDS No. 44-1418).
Figure S3. Influence of annealing temperatures (600 °C, 700 °C and 800 °C in N₂ for 2h, ramping rate: 5 °C/min) on phase purity of coherent Ni₃S₂/C nanocomposite. Results indicate Ni₃S₂ can be a more stable phase in nickel sulfides and high temperature is helpful to form phase-purity Ni₃S₂/C.

Figure S4. (a) TGA result of “Ni(NO₃)₂ + thiourea + citric acid + NaCl” composites at temperatures ranging from room temperature to 800 °C in N₂ with a heating rate of 5 °C/min; (b) SEM image of Ni₃S₂/C synthesized by l-cysteine
Figure S5. Low magnification SEM images of (a) bare Ni$_3$S$_2$ without adding the carbon precursor, confirming the carbon can provide abundant surfaces for reactions and prevent Ni$_3$S$_2$ nanoparticles from agglomeration during the annealing process; (b) bulk Ni$_3$S$_2$+C without adding NaCl templates, showing a key role of NaCl templates plays an indispensable role in the formation of homogeneous coherent nanostructures; (c) XRD results of bare Ni$_3$S$_2$, bulk Ni$_3$S$_2$+C and coherent Ni$_3$S$_2$/C, indicating that phase purity of as-prepared samples.
Figure S6. XRD pattern of coherent Ni$_3$S$_2$/C nanocomposite after TGA measurement in air (20 °C to 700 °C, ramping rate: 10 °C/min), indicating Ni$_3$S$_2$ transfer completely into NiO (JCPDS No. 47-1049).

Figure S7. (a) Nitrogen sorption isotherms of coherent Ni$_3$S$_2$/C composites, bulk Ni$_3$S$_2$+C and bare Ni$_3$S$_2$, the BET surface areas were determined by a multi-point-BET method; Pore size distribution of (b) bulk Ni$_3$S$_2$+C and (c) bare Ni$_3$S$_2$, the pore volumes were determined by BJH-Desorption method.
Figure S8. CV curves of coherent Ni$_3$S$_2$/C in lithium ion batteries under a scan rate of 0.2 mV/s. Electrolyte was 1 M LiPF$_6$ in EC/DEC/FEC, 1:1:0.05 in volume %.

In the first scan, two cathodic peaks at 1.05 V and 0.45 V and one anodic peak at 2.02 V can be clearly distinguished. The peak located at 1.05 V can be ascribed to the insertion of lithium ion into Ni$_3$S$_2$. The broad peak at about 0.45 V might be the conversion reaction as well as the formation of SEI and decomposition of electrolyte, which corresponded well with that of SIBs. After activating in the first cycle, one couple at 1.22 V / 2.09 V could be recognized. Total electrochemical reaction can be described in Equation (1). The potential is similar to that of sodium ion batteries.

$$\text{Ni}_3\text{S}_2 + 4 \text{Li}^+ + 4 e^- \leftrightarrow 3 \text{Ni} + 2 \text{Li}_2\text{S}$$  \hspace{1cm} (1)

Figure S9. Discharge/charge curves of bare carbon networks under 0.1 A/g in 0 ~ 3 V, which shows a low coulombic efficiency of 34 %.
Figure S10. Volumetric capacity of coherent Ni$_3$S$_2$/C electrode under 0.1 A/g. The calculation is based on whole anode coating volume.

Figure S11. Rate performances of pure carbon matrix.
Figure S12. (a) Schematic Illustration and optical photograph in different steps of preparing Na$_3$V$_2$(PO$_4$)$_3$/rGO via sol-gel and post-annealing methods; (b) SEM of Na$_3$V$_2$(PO$_4$)$_3$/rGO lamellar structure with multi-stacked structures, (c) Cyclic performance and efficiencies of Na$_3$V$_2$(PO$_4$)$_3$/rGO at 2 C for 100 cycles (1 C = 110 mA g$^{-1}$; the inset is the charge/discharge curves at 1$^{st}$, 2$^{nd}$, 5$^{th}$ and 100$^{th}$ cycles, flat charge and discharge plateaus at around 3.3 and 3.5 V, corresponding to the redox pair of V$^{3+}$/V$^{4+}$).
Figure S13. Illustration of the composition and cycling performance of Na$_3$V$_2$(PO$_4$)$_3$/rGO cathode || Ni$_3$S$_2$/C anode full cell at 0.5 A g$^{-1}$ (the inset is the charge/discharge curves at 1$^{st}$, 2$^{nd}$, 5$^{th}$ cycles, The open potential of fresh full-cell is about 0.5 V, which may be caused by the high internal resistance; mass ratio between cathode and anode was 6:1).

Figure S14. Cyclic voltammetry curves of (a) the bulk Ni$_3$S$_2$+C electrode and (c) bare Ni$_3$S$_2$ electrode at different scan rates; $I$ as a function of $v$ for (b) bulk Ni$_3$S$_2$+C electrode and (d) bare Ni$_3$S$_2$ electrode. For bulk Ni$_3$S$_2$+C electrode, the D is $5 \times 10^{-13}$ and $4.5 \times 10^{-13}$ cm$^2$ g$^{-1}$ for anodic peak and cathodic peak, respectively. For bare Ni$_3$S$_2$ electrode, the D is $3.6 \times 10^{-13}$ and $5.2 \times 10^{-13}$ cm$^2$ g$^{-1}$ for anodic peak and cathodic peak, respectively.
Figure S15. Nyquist plots of coherent Ni$_3$S$_2$/C composites, bulk Ni$_3$S$_2$+C and bare Ni$_3$S$_2$ after 135 cycles under various rates, the coherent structure has lowest charge-transfer resistance and fastest sodium ion diffusion among listed three samples.

Figure S16. XRD patterns of electrodes at charge state (3.0 V) for bulk Ni$_3$S$_2$+C and bare Ni$_3$S$_2$. Results indicate the irreversible reactions of bulk Ni$_3$S$_2$+C and bare Ni$_3$S$_2$ after first cycle, demonstrating the key role of coherent structure to reversible reactions.
Figure S17. Cyclic performances of coherent Ni$_3$S$_2$/C, bulk Ni$_3$S$_2$ + C and bare Ni$_3$S$_2$ under a low current density of 0.1 A/g.
Table S1. Comparison of specific capacity and capacity retention at different current densities for Ni$_3$S$_2$ composite electrode with other Ni$_3$S$_2$ based anodes in SIBs.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Voltage range (V)</th>
<th>Current density (A/g)</th>
<th>Cycle number</th>
<th>Specific capacity after cycle (mAh/g)</th>
<th>Capacity retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coherent Ni$_3$S$_2$/C networks (This work)</td>
<td>0.01–3.0</td>
<td>0.1</td>
<td>100</td>
<td>453</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.4</td>
<td>100</td>
<td>430</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>200</td>
<td>409</td>
<td>96</td>
</tr>
<tr>
<td>PEDOT@Ni$_3$S$_2$ on Ni foam [ref 30]</td>
<td>0.5–2.8</td>
<td>0.6</td>
<td>50</td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Nickel sulfide nanoparticles with an ultrathin carbon layer [ref 31]</td>
<td>0.01–3.0</td>
<td>0.1</td>
<td>200</td>
<td>340</td>
<td>85</td>
</tr>
<tr>
<td>Layered nickel sulfide-reduced graphene oxide [ref 32]</td>
<td>0.005–3.0</td>
<td>0.1</td>
<td>50</td>
<td>392</td>
<td>76</td>
</tr>
<tr>
<td>Different morphologies of Ni$_3$S$_2$ on Ni foam [ref 33]</td>
<td>0.01–3.0</td>
<td>0.05</td>
<td>100</td>
<td>315</td>
<td>85</td>
</tr>
</tbody>
</table>