Supporting Information

Inorganic Gel-Derived Metallic Frameworks

Enabling High-Performance Silicon Anodes

Anping Zhang,†§ Zhiwei Fang,†§ Yawen Tang,† Yiming Zhou,† Ping Wu,*,† and Guihua Yu*,‡

†Jiangsu Key Laboratory of New Power Batteries, Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023, China

‡Materials Science and Engineering Program and Department of Mechanical Engineering, The University of Texas at Austin, Austin, Texas 78712, United States

§A.Z. and Z.F. contributed equally to this work.

*E-mail: ghyu@austin.utexas.edu

*E-mail: zjuwuping@njnu.edu.cn
Experimental Methods

Synthesis of the Si@Sn–Ni hybrid cyanogel: Commercial Si particle (~50 nm) was purchased from Alfa Aesar. Solution A was diethylene glycol (DEG) solution containing 5 mg mL\(^{-1}\) Si particles and 0.2 mol L\(^{-1}\) SnCl\(_4\). Solution B was DEG solution containing 5 mg mL\(^{-1}\) Si particles and 0.2 mol L\(^{-1}\) K\(_2\)Ni(CN)\(_4\). The Si@Sn–Ni hybrid cyanogel was conveniently obtained by mixing solutions A and B with a volume ratio of 1:1 at 50 °C. Sn–Ni cyanogel was also prepared without adding Si particles while keeping the other conditions unchanged.

Synthesis of the Si@Sn–Ni all-metal framework: The Si@Sn–Ni framework was synthesized through a facile and scalable gel-reduction route using Si@Sn–Ni hybrid cyanogel as a precursor and NaBH\(_4\) as a reductant. Specifically, a DEG solution containing 2 mol L\(^{-1}\) NaBH\(_4\) was added to the Si@Sn–Ni cyanogel at 50 °C, and the reaction system was allowed to stand for 2 h. The solid product was washed and dried in a vacuum oven, yielding the final Si@Sn–Ni all-metal framework. For comparison, Sn–Ni alloy framework was obtained through a similar wet-chemical reduction process by using Sn–Ni cyanogel as a precursor, instead of Si@Sn–Ni hybrid cyanogel.

Characterization: The morphological, compositional, and structural features of the products were characterized by X-ray powder diffraction (XRD, Rigaku D/max 2500/PC), scanning electron microscope (SEM, HITACHI SU8200), and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F, 200 kV) coupled with an energy-dispersive X-ray spectrometer (EDS, Thermo Fisher Scientific). Nitrogen adsorption/desorption tests were performed at 77 K using a Micromeritics ASAP 2020 analyzer. X-ray photoelectron spectroscopy (XPS) test was examined on an ESCALAB 250Xi Spectrometer (Thermo Fisher Scientific). Raman spectra were conducted on a LabRam HR800 spectrometer.
**Electrochemical measurements**: The lithium storage performance of the products was tested using 2025-type half coin cells, assembled in an argon-filled glove box (Innovative Technology, IL-2GB). The working electrodes were prepared using copper foil current collectors, coated beforehand with aqueous slurries containing active materials (e.g., Si@Sn–Ni framework), conductive material (carbon black), and binder (sodium carboxymethyl-cellulose) in a weight ratio of 70:15:15. Subsequently, the obtained electrodes were dried in a vacuum oven (120 °C, 12 h). The mass loading of active materials on copper foils was ~1 mg cm\(^{-2}\). The calculation method for the specific capacities is based on the entire Si@Sn–Ni framework anodes. The half cells were assembled with lithium foil as the counter electrode, and 1 M LiPF\(_6\) in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 in volume) containing 5 vol\% fluoroethylene carbonate (FEC) additive as the electrolyte. The cycling and rate performances of these products were cycled between 0.01 and 1.2 V vs. Li/Li\(^+\) (0.1 A g\(^{-1}\) for the first cycle and 0.5 to 10 A g\(^{-1}\) for subsequent cycles). Cyclic voltammetry (CV) measurements were carried out on a CHI 660B electrochemical workstation in the potential range of 0-1.2 V vs. Li/Li\(^+\) at a scan rate of 0.2 mV s\(^{-1}\). Electrochemical impedance spectroscopy (EIS) data were operated on a CHI 660B electrochemical workstation over the frequency range of 100 kHz to 10 mHz.
Figure S1. Synthetic diagram of the Sn–Ni alloy framework.
Figure S2. (a) Photograph of the Sn–Ni cyanogel. (b) TEM image, (c) XRD pattern, (d) EDS spectrum, and (e) elemental mappings of the Sn–Ni alloy framework.
Figure S3. (a) TEM image and HRTEM image (inset) and (b) micro-area EDS spectra of the Si@Sn–Ni all-metal framework.
Figure S4. Elemental mappings of the Si@Sn–Ni all-metal framework in a low magnification.
Figure S5. (a) Nitrogen adsorption/desorption isotherms and (b) pore size distribution of the Si@Sn–Ni framework.
Figure S6. Si 2p XPS spectrum of the Si@Sn–Ni all-metal framework (curve $b$) compared with Si particles (curve $a$).
Figure S7. The initial three CV curves of the Si particles (a) and Sn–Ni alloy framework (b).
Figure S8. The initial discharge and charge curves for the Si@Sn–Ni all-metal framework in comparison with Si particles and Sn–Ni alloy framework.
Figure S9. The cycling stability (a) and rate capability (b) of the Si/Sn–Ni mixture in comparison with Si@Sn–Ni framework.
Figure S10. Photographs of the Si@Sn–Ni hybrid cyanogels with different silicon concentrations: (a) 2.5 mg mL\(^{-1}\), (c) 5 mg mL\(^{-1}\), and (e) 10 mg mL\(^{-1}\). EDS spectra of the Si@Sn–Ni frameworks prepared with different Si concentrations: (b) 2.5 mg mL\(^{-1}\), (d) 5 mg mL\(^{-1}\), and (f) 10 mg mL\(^{-1}\).
Figure S11. The cycling stability (a) and rate capability (b) of the Si@Sn–Ni frameworks prepared with different Si concentrations: 2.5 mg mL$^{-1}$, 5 mg mL$^{-1}$, and 10 mg mL$^{-1}$.

As seen from Figure S10, the Si/Sn atomic ratio of the Si@Sn–Ni frameworks prepared with different Si concentrations is determined to be 1.1:1 (2.5 mg mL$^{-1}$), 2.2:1 (5 mg mL$^{-1}$), and 3.9:1 (10 mg mL$^{-1}$), respectively, whereas Sn/Ni atomic ratio is determined to be about 1.9:1 (Figure S2d). Thus, in these Si@Sn–Ni frameworks, the mass fraction of Si can be calculated to be 17.1 wt% (2.5 mg mL$^{-1}$), 29.2 wt% (5 mg mL$^{-1}$), and 42.3 wt% (10 mg mL$^{-1}$), respectively, whereas the mass fraction of Sn can be calculated to be 65.8 wt% (2.5 mg mL$^{-1}$), 56.2 wt% (5 mg mL$^{-1}$), and 45.8 wt% (10 mg mL$^{-1}$), respectively. The theoretical capacities of active Si and Sn are 3579 mA h g$^{-1}$ ($\text{Li}_15\text{Si}_4$, room temperature) and 994 mA h g$^{-1}$ ($\text{Li}_{22}\text{Sn}_5$), respectively, whereas Ni is inactive and does not contribute to reversible capacities. Therefore, the theoretical capacity of the Si@Sn–Ni frameworks prepared with different Si concentrations can be calculated to be 1266 mA h g$^{-1}$ (2.5 mg mL$^{-1}$), 1605 mA h g$^{-1}$ (5 mg mL$^{-1}$), and 1969 mA h g$^{-1}$ (10 mg mL$^{-1}$), respectively.
Table S1 Comparison of reversible capacity and capacity retention between Si@Sn–Ni all-metal framework and previous Si–M anodes including Si–M’ (M’=Sn, Sb, Ge) and Si–M” (M”=Ni, Fe, Cu, Ti) ones. (Note: n/m refers to the reversible capacity in n cycles versus m cycles.)

<table>
<thead>
<tr>
<th>Anode materials</th>
<th>Reversible capacity (mAh g⁻¹)</th>
<th>Capacity retention (n/m)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si@Sn–Ni all-metal framework</td>
<td>1205 at 0.5 A g⁻¹ (100 cycles)</td>
<td>86% (100/2)</td>
<td>This work</td>
</tr>
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<td>Si–Sn nanocomposites</td>
<td>828 at 0.3 A g⁻¹ (100 cycles)</td>
<td>56% (100/2)</td>
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<tr>
<td>Si–Sn composite</td>
<td>935 at 0.4 A g⁻¹ (50 cycles)</td>
<td>78% (50/3)</td>
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<tr>
<td>nanoporous Si–Sb alloy</td>
<td>647 at 0.1 A g⁻¹ (90 cycles)</td>
<td>78% (90/2)</td>
<td>3</td>
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<tr>
<td>nanoporous Si–Ge alloy</td>
<td>1372 at 0.1 A g⁻¹ (80 cycles)</td>
<td>68% (80/2)</td>
<td>4</td>
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<tr>
<td>Si–Ge alloy nanoparticles</td>
<td>977 at 0.5 A g⁻¹ (100 cycles)</td>
<td>78% (100/2)</td>
<td>5</td>
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<tr>
<td>Si–Ge nanowires</td>
<td>964 at 0.8 A g⁻¹ (50 cycles)</td>
<td>72% (50/2)</td>
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<tr>
<td>Si/Ge nanowire arrays</td>
<td>1500 at 0.4 A g⁻¹ (100 cycles)</td>
<td>70% (100/2)</td>
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<td>Si/Ni composites</td>
<td>474 at 0.2 A g⁻¹ (100 cycles)</td>
<td>78% (100/4)</td>
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<td>NiSi₂ nanocrystalline</td>
<td>395 at 0.4 A g⁻¹ (60 cycles)</td>
<td>85% (60/2)</td>
<td>9</td>
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<td>FeSi₂ nanoparticles</td>
<td>980 at 0.4 A g⁻¹ (50 cycles)</td>
<td>63% (50/2)</td>
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<td>Si–Fe nanocomposite</td>
<td>641 at 0.4 A g⁻¹ (115 cycles)</td>
<td>94% (115/2)</td>
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<tr>
<td>Si/Cu composite</td>
<td>1305 at 0.2 A g⁻¹ (150 cycles)</td>
<td>56% (150/2)</td>
<td>12</td>
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<td>Ti@Si nanorod arrays</td>
<td>1125 at 0.2 A g⁻¹ (30 cycles)</td>
<td>56% (30/2)</td>
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<td>Si–Ti binary framework</td>
<td>1161 at 0.5 A g⁻¹ (100 cycles)</td>
<td>79% (100/2)</td>
<td>14</td>
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</tbody>
</table>
References