Supplementary Information

In-Situ Growth of MOFs on the Surface of Si Nanoparticles for Highly Efficient Lithium Storage: Si@MOF Nanocomposites as Anode Materials for Lithium-Ion Batteries

Yuzhen Han,†⊥ Pengfei Qi,†⊥ Xiao Feng,† Siwu Li,† Xiaotao Fu,† Haiwei Li,† Yifa Chen,† Junwen Zhou,‡ Xingguo Li‡ and Bo Wang***

†Key Laboratory of Cluster Science, Ministry of Education of China, School of Chemistry, Beijing Institute of Technology, 5 South Zhongguancun Street, Beijing, 100081, P.R. China.
‡College of Chemistry and Molecular Engineering, Peking University, 5 Yiheyuan Road, Beijing, 100871, P.R. China.

E-mail: bowang@bit.edu.cn
Experimental section

Synthesis Si@ZIF-8 nanocrystals were synthesized through a simple mechanochemical synthetic protocol. Reactions were carried out in a ball mill (QM-3B, Nanjing University Instrument Factory, China) using a 80 mL stainless steel grinding jar with five 10 mm steel balls. A solid mixture of zinc oxide (ZnO, 0.814 g, 10 mmol), nano Si (0.14g, 5 mmol), 2-methylimidazole (1.6422 g, 20 mmol) and 1mL methanol was placed into the jar and ground at high speed for 30 min. The products were washed with methanol (30 mL) for three times and dried at 85 °C.(All the reagents come from J & K and the solvent comes from Beijing Chemical Reagent, the nano Si powder comes from Shanghai Chaowei Nano Technology. The as-prepared Si@ZIF-8 was transferred to a tube furnace and was heat-treated at target temperatures (700 °C) for 1 h under nitrogen with a heating rate of 5 °C min⁻¹ to pyrolyze the nanocrystals. After that, the materials were cooled down to room temperature naturally.

Characterization Powder X-ray diffraction (PXRD) pattern was analyzed with monochromatized Cu-Kα (λ = 1.54178 Å) incident radiation by a D8 Advance Bruker powder diffractometer operating at 40 kV voltage and 50 mA current. Nitrogen sorption isotherms were measured at 77 K on a Quantachrome Instrument Autosorb-IQ2 after pretreatment by heating the samples under vacuum at 120 °C for 6 h before the measurement. ICP (Inductive Coupled Plasma Emission Spectrometer) was tested by Varian 725 inductively coupled plasma emission spectrometer. Elemental analysis was analyzed by Vario EL III. Scanning electron microscopy
(SEM and EDX; JSM7000 instrument, JEOL). Transmission electron microscopy (TEM) was tested by JEM-2100 at 200kV. X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALab 250Xi using 200 W monochromated Al Ka radiation. The 500 µm X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about $3 \times 10^{-10}$ mbar. Typically the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing.

**Electrochemical test** To prepare the anodes, 60 wt% active material, 20 wt% Super P carbon black and 20 wt% sodium alginate binder were mixed in water solution to form a slurry. The slurry was cast onto copper foil and dried under a vacuum at 120°C for 12h. Coin cells of CR2032 type were constructed inside an argon-filled glove box using a lithium metal foil as the negative electrode and the composite positive electrode separated by polypropylene microporous separator (Celgard). The electrolyte used was 1 M LiPF$_6$ in ethyl carbonate (EC), diethyl carbonate (DMC) and Ethyl methyl carbonate (EMC) (1:1:1 in v/v/v). Assembled coin cells were allowed to soak overnight and then were charged and discharged between 0.02 and 3.0 V using a Land battery tester at ambient temperature. The cyclic voltammetry of active materials were recorded with a potentiostat. (CHI 760E: CH Instrumental Inc.) The range of voltage was 20 mV – 3.0 V with a scan rate of 0.1 mV /s. The electrochemical impedance spectra were measured using a potentiostat (CHI 760E: CH Instrumental Inc.) after 5 cycles at 50 mA g$^{-1}$. The frequency range was from $10^{-1}$ to $10^4$ Hz with an applied voltage of 0.2V.
Table S1. Elemental composition analyzed by different methods (wt%)

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>Si</th>
<th>C</th>
<th>N</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental Analysis</td>
<td>30.7(^a)</td>
<td>7.3(^a)</td>
<td>36.3(^b)</td>
<td>21.8(^b)</td>
<td>3.8(^b)</td>
</tr>
<tr>
<td>XPS</td>
<td>13.4</td>
<td>0.4</td>
<td>52.2</td>
<td>12.7</td>
<td></td>
</tr>
<tr>
<td>EDX</td>
<td>11.7</td>
<td>3.9</td>
<td>55.5</td>
<td>20.7</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) The content of Zn and Si is analyzed by inductively coupled plasma atomic emission spectrometer (ICP); \(^b\) The C, N, H are analyzed by general elemental analysis.

Figure S1. XPS spectra of a) Si@ZIF-8-700N, b) C 1s narrow scan of Si@ZIF-8-700N, c) N 1s narrow scan of Si@ZIF-8-700N, d) Si 2p narrow scan of Si@ZIF-8-700N.
Figure S2. The pore size distributions from NLDFT calculations using the adsorption branches, (a) Si@ZIF-8 and (b) Si@ZIF-8-700N.

Figure S3. Nitrogen sorption isotherms at 77 K of Si.
Figure S4. SEM images of a) pure Si; b) Si@ZIF-8; HRTEM images of c) pure Si; d) Si@ZIF-8.

Figure S5. TEM images of (a) pure nano Si and (b) ZIF-8 synthesized by ball milling.
Figure S6. Cycle-life performances of Si@ZIF-8-700N, ZIF-8-700N and pure nano Si. Si@ZIF-8 sample has the highest capacity and cycling stability. “700N” denotes a sample heated at 700 °C under a nitrogen atmosphere for one hour.

Figure S7. (a) PXRD and (b) Cycle-life performance of Si@ZIF-8-2-700N (Si@ZIF-8-2-700N denotes the twice addition amount of Si)
Figure S8. PXRD data of ball milled ZIF-8.

Figure S9. Nyquist plots for ZIF-8-700N after four cycles.

Figure S10. (a) PXRD of anode pole and the anode pole after 30 cycles; (b) FT-IR of ZIF-8, Si@ZIF-8 and ZIF-8-700N; (c) FT-IR of Si@ZIF-8 and Si@ZIF-8 after 30 cycles. The IR spectrum of carbonized sample (Fig. S11b) shows that most of the peaks related to C-H vibrations are disappeared, and the peaks attributed to C=C, C=N, C-C and C-N vibrations are broadened.
Figure S11. Cycle-life performances of Si@ZIF-8 without carbonized.

Figure S12. CV test of the first 3 cycles.