Wet-chemical Synthesized MCMB@Si@C Microspheres for High-performance Lithium-ion Battery Anodes

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Supporting Figures

Supplementary Scheme S1. Schematic images of the synthesis of the MCMB@Si microspheres.

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**Supplementary Fig. S1.** (a) XPS spectra of the MCMB and carboxylated MCMB, (b) XPS spectra of the Si and APS-Si, (d) XPS spectra of MCMB@Si and MCMB@Si@C.

**Supplementary Fig. S2.** XRD patterns of MCMB, Si and MCMB@Si.
Supplementary Fig. S3. Raman spectra of MCMB@Si.

Supplementary Fig. S4. Low-magnification TEM image of APS-Si; b) HRTEM image of an APS-Si.
Supplementary Fig. S5. Cycling performance of a) MCMB and MCMB@C; b) MCMB-COOH and MCMB-COOH@C; c) Si-OH and Si-OH@C; d) APS-Si and APS-Si@C.

Supplementary Fig. S6. a) N2 adsorption/desorption isotherms of carboxylated MCMB, MCMB@Si and MCMB@Si@C; b) Pore size distribution curves of the three samples.
<table>
<thead>
<tr>
<th>Sample name</th>
<th>M0</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
<th>M5</th>
<th>M6</th>
<th>M7</th>
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<tr>
<td>Sample mass (mg)</td>
<td>8.40</td>
<td>4.60</td>
<td>7.20</td>
<td>7.10</td>
<td>6.00</td>
<td>6.80</td>
<td>5.10</td>
<td>4.50</td>
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<tr>
<td>Concentration of Si (ppm)</td>
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<td>2.14</td>
<td>4.18</td>
<td>5.53</td>
<td>6.88</td>
<td>11.11</td>
<td>10.55</td>
<td>11.67</td>
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<tr>
<td>Si mass fraction (%)</td>
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<td>4.65</td>
<td>5.80</td>
<td>7.79</td>
<td>11.47</td>
<td>16.34</td>
<td>20.69</td>
<td>25.93</td>
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**Supplementary Table S1.** ICP test information of MCMB@Si@C with different Si contents.

**Supplementary Fig. S7.** TGA analysis of MCMB@Si@C with different Si contents.
**Supplementary Fig. S8.** Low-resolution SEM images of a) MCMB@Si and b) MCMB/Si.

**Supplementary Fig. S9.** Nyquist plots of MCMB@Si@C and MCMB/Si@C obtained by applying a sine wave over the frequency range from 100 kHz to 0.01 Hz.
Supplementary Fig. S10. Cyclic curves for the MCMB@Si@C electrodes between 1.5 V and 0.01 V versus Li/Li⁺ at the scan rate of 0.1 mV s⁻¹.

Supplementary Fig. S11. a) Low-magnification SEM image of MCMB@Si@C after 100 cycles; b) High-magnification SEM image of MCMB@Si@C after 100 cycles.

Supplementary note: Experimental section

1. Materials

Si nanoparticles (80-100 nm, Aladdin, China), mesocarbon microbeads (MCMB, 20 μm, Sichuan Kaiyuan Huineng New material technology Ltd., China),
Aminopropyl) trimethoxy-silane (APS, 97%, Sigma-Aldrich, America), HNO₃ (AR, Aladdin, China), H₂SO₄ (AR, 98%, Sinopharm Chemical Reagent Co., Ltd., China), H₂O₂ (AR, 30%, Sinopharm Chemical Reagent Co., Ltd., China), super P carbon black (CP, Sinopharm Chemical Reagent Co., Ltd., China), sodium carboxymethyl cellulose (~90000, Sigma-Aldrich, America), electrolyte solution (Dongguan shanshan battery materials co.,ltd, China), Fluoroethylene carbonate (>98%, Aladdin, China), were used in our experiments.

2. Synthesis of MCMB@Si@C microspheres and MCMB/Si@C composites

MCMB@Si microspheres were prepared by a wet-chemical process. All chemicals, including silicon nanoparticles and MCMB, were used without any further purification. Firstly, 1 g silicon nanoparticles were added hydroxyl on the surface by treated with 40 mL solution (H₂SO₄: H₂O₂ = 1:1 in volume) for 10 min, and 10 g MCMB was added carboxyl on the surface by hydrothermally treated with 20 mL HNO₃ at 180 °C for 10 h in a hydrothermal reactor. Then, various ratio modified MCMB and modified silicon nanoparticles (200 mg MCMB with 20, 30, 40, 50, 60, 70 and 80 mg silicon nanoparticles respectively) and 80 μL APS were added into 20 mL deionized water under magnetic stirring for 2 h. Subsequently, MCMB@Si materials were collected after centrifuging process by deionized water for three times. Finally, the MCMB@Si@C structures, with various Si contents, were achieved via chemical vapor decomposition (CVD) process of acetylene gas at 650 °C for 2 h. As a comparison, modified MCMB and modified Si were physically mixed in 20 mL deionized water without APS for 2 h. Then, MCMB/Si@C composites were acquired via CVD process of acetylene gas at 650 °C for 2 h.

3. Characterization

The morphology of as-prepared samples was characterized by field emission scanning electron microscopy (FESEM, HITACH S4800) and transmission electron microscopy (TEM, PHILIPS F200). Energy dispersive spectroscopy (EDS) mapping image was represented by a Tecnai G2 F20 ChemiSTEM attached with an Oxford X-Max 80T EDX detector system. X-ray photoelectron spectroscopy (XPS) was measured...
by employing a Thermo ESCALAB 250Xi spectrometer with a monochromatic Al Kα line (1486.6 eV). The crystal structures of materials were measured by a high power X-ray diffractometer (XRD) on a Rigaku D/max-ga X-ray diffractometer, where the Cu K radiation was 1.54 Å. The Raman spectra were tested on a HR800 Raman spectrometer using the 514 nm line of an Ar ion laser operated at 10 mW. The content of Si was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, iCAP 6300). The mass content of carbon layer was confirmed by Thermogravimetric analysis (TGA) using a SDT Q600 V8.2 Build 100.

4. Electrochemical characterization

The coin-type half cells, composed of MCMB@Si@C microstructures as the working electrode and lithium metal as the counter electrode, were encapsulated in a glove box (Mbraun, labstar, Germany) under argon atmosphere. The slurry casting on the Cu collector was constituted of active materials (MCMB@Si@C with various Si contents and MCMB/Si @C), sodium carboxymethyl cellulose (CMC) and super P carbon black, with the mass ratio of 7:2:1. The electrolyte was LiPF₆ in dimethyl carbonate (DMC) and ethylene carbonate (EC) (1:1 at volume ratio) with 10 vol% fluoroethylene carbonate (FEC) as additive. Cyclic voltammetry (CV) curve was measured on an Arbin BT 2000 system at a scan rate of 0.1 mVs⁻¹. Nyquist plot was also tested on the Arbin BT 2000 system in the frequency range from 100 kHz to 100 mHz. The Galvanostatic discharge-charge data was conducted by a Land CT2001A system in the potential range of 0.001~1.5 V.