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.

Sample name	M 0	M1	M2	M3	M4	M5	M6	M7
Sample mass (mg)	8.40	4.60	7.20	7.10	6.00	6.80	5.10	4.50
Concentration of Si (ppm)	0.26	2.14	4.18	5.53	6.88	11.11	10.55	11.67
Si mass fraction (%)	0.32	4.65	5.80	7.79	11.47	16.34	20.69	25.93

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 sing 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





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), (3-

Aminoprupyl) 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 (H_2SO_4 : $H_2O_2 = 1$: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 μ L 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 Ka line (1486.6eV). 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.