Electronic Supplementary Information

Scalable and controllable fabrication of CNTs improved yolk-shelled Si anode with advanced in-operando mechanical quantification

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Fig. S1. SEM images of ZIF-Si. a, ZIF-8-Si. b, ZIF-67/ZIF-8-Si. c, ZIF-8/ZIF-67-Si. d, ZIF-67-Si. Scale bar: 1 µm. All of the ZIF-Si samples are dodecahedron-shaped microcrystals with sizes ranged from 1.0 to 5.0 µm.
Fig. S2. XRD patterns of ZIF-Si samples. All observed peaks from the ZIF-Si samples can be assigned to ZIF-67, ZIF-8 and Si.
Fig. S3. Morphological and structural characteristics of Si/C. (a, b), Cross-sectional SEM and TEM images of Si/C shell (Scale bar: 100 nm). c, SEM image of a broken Si/C unit (Scale bar: 500 nm). d, Low magnification TEM image of Si/C (Scale bar: 500 nm).
Fig. S4. a, TEM image of Si/C. (b-e), EDS mapping images of Si/C. Scale bar: 200 nm.
Fig. S5. a, XRD patterns of Si/C and Si/C-CNT samples. b, Raman spectra of Si/C and Si/C-CNT samples.
Fig. S6. Morphological and structural characteristics of Si/C-CNT#1. (a, b), Cross-sectional SEM and TEM images of Si/C-CNT#1 shell (Scale bar: 100 nm). c, SEM image of a broken Si/C-CNT#1 unit (Scale bar: 500 nm). d, Low magnification TEM image of Si/C-CNT-1 (Scale bar: 500 nm).
Fig. S7. a, TEM and (b-f), EDS mapping images of Si/C-CNT#1. Scale bar: 200 nm.
Fig. S8. a, HRTEM and (b-d), EDS mapping images of CNTs-Co₃O₄ NPs on the outer surface of Si/C-CNT#1. Scale bar: 20 nm.
Fig. S9. XRD patterns of Si/C-CNT samples before air oxidation treatment.
**Fig. S10.** Morphological and structural characteristics of Si/C-CNT#2. (a, b), Cross-sectional SEM and TEM images of Si/C-CNT#2 shell (Scale bar: 100 nm). c, SEM image of a broken Si/C-CNT#2 unit (Scale bar: 500 nm). d, Low magnification TEM image of Si/C-CNT-2 (Scale bar: 1 μm).
Fig. S11. a, TEM and (b-f), EDS mapping images of Si/C-CNT#2. Scale bar: 500 nm.
**Fig. S12.** a, HRTEM and (b-d), EDS mapping images of CNTs-Co$_3$O$_4$ NPs on the inner surface of Si/C-CNT#2. Scale bar: 20 nm.
**Fig. S13.** Morphological and structural characteristics of Si/C-CNT#3. (a, b), Cross-sectional SEM and TEM images of Si/C-CNT#3 shell (Scale bar: 100 nm). c, SEM image of a broken Si/C-CNT#3 unit (Scale bar: 500 nm). d, Low magnification TEM image of Si/C-CNT-3 (Scale bar: 1 µm).
Fig. S14. a, TEM and (b-f), EDS mapping images of Si/C-CNT#3. Scale bar: 500 nm.
Fig. S15. a, HRTEM and (b-d), EDS mapping images of CNTs-Co$_3$O$_4$ NPs on the outer surface of Si/C-CNT#3. Scale bar: 20 nm.
Fig. S16. HRTEM and (b-d), EDS mapping images of CNTs-Co$_3$O$_4$ NPs on the inner surface of Si/C-CNT#3. Scale bar: 20 nm.
Fig. S17. Initial discharge-charge profiles of a, Si/C, b, Si/C-CNT#1, c, Si/C-CNT#2 and d, Si/C-CNT#3. Voltage range: 0.01 V–3.0 V. Current density: 0.1 A g⁻¹.
Fig. S18. Nyquist plots of Si/C and Si/C-CNT samples.
**Fig. S19.** SEM images of a, Si/C, b, Si/C-CNT#1, c, Si/C-CNT#2 and d, Si/C-CNT#3 after cycling test. Scale bar: 1 μm. Inserts are the SEM image of samples before cycling test. Scale bar: 500 nm.
Fig. S20. CVs of Si/C-CNT#3 at different scan rates from 0.1 to 1.0 mV s⁻¹ within a voltage range of 0.01–3.0 V.
**Fig. S21.** In-operando recorded TEM image for a cluster of Si/C-CNT#3 units immobilised on the copper grid-working electrode. Red line enclosed area indicates the targeted set of Si NPs inside a Si/C-CNT#3 unit. Scale bar: 500 nm.
Fig. S22. a, Time-lapsed in-operando TEM images of the targeted cluster of Si/C-CNT#1 units during lithiation (0-180 s)/delithiation (180-360 s). b, Load- and displacement-time profiles during lithiation/delithiation. Scale bar: 500 nm.
Fig. S23. a, Time-lapsed in-operando TEM images of the targeted cluster of Si/C-CNT#2 units during lithiation (0-180 s)/delithiation (180-360 s). b, Load- and displacement-time profiles during lithiation/delithiation. Scale bar: 500 nm.
Fig. S24. Assembled TEM electrochemical measurement cell before inducing Li dendrite. Red line enclosed area shows the in-situ TEM viewing zone on a Si/C-CNT#3 structure unit. Scale bar: 1 μm.
Fig. S25. **a**, Time-lapsed in-operando TEM images of Si/C-CNT#3 during the first 10 s of Li plating process. Scale bar: 500 nm. **b**, Corresponding load- and displacement-time profiles.
**Fig. S26.** Time-lapsed in-operando TEM images of the Si/C-CNT#3 during Li plating process between 60 and 95 s. Scale bar: 500 nm.
**Fig. S27.** a, Time-lapsed in-operando TEM images of the Si/C-CNT#3 during Li plating process between 95 and 99 s. Scale bar: 500 nm. b, Corresponding load- and displacement-time profiles.
Fig. S28. a, Time-lapsed in-operando TEM images of the Si/C-CNT#3 during Li plating process between 100 and 300 s. Scale bar: 500 nm. b, Corresponding load- and displacement-time profiles.
Fig. S29. Time-lapsed in-operando high magnification TEM images showing Li dendrites dissolution process. Scale bar: 100 nm.