Electronic Supplementary Information

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

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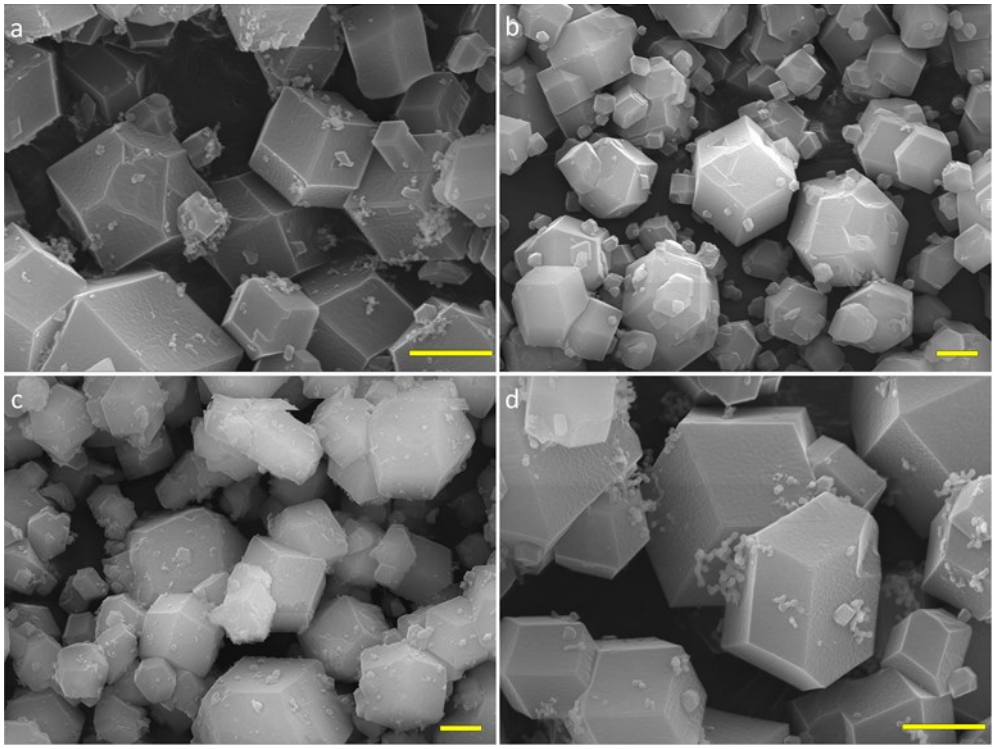

Fig. S1. SEM images of ZIF-Si. **a**, ZIF-8-Si. **b**, ZIF-67/ZIF-8-Si. **c**, ZIF-8/ZIF-67-Si. **d**, ZIF-67-Si. Scale bar: 1 μm. All of the ZIF-Si samples are dodecahedron-shaped microcrystals with sizes ranged from 1.0 to 5.0 μm.

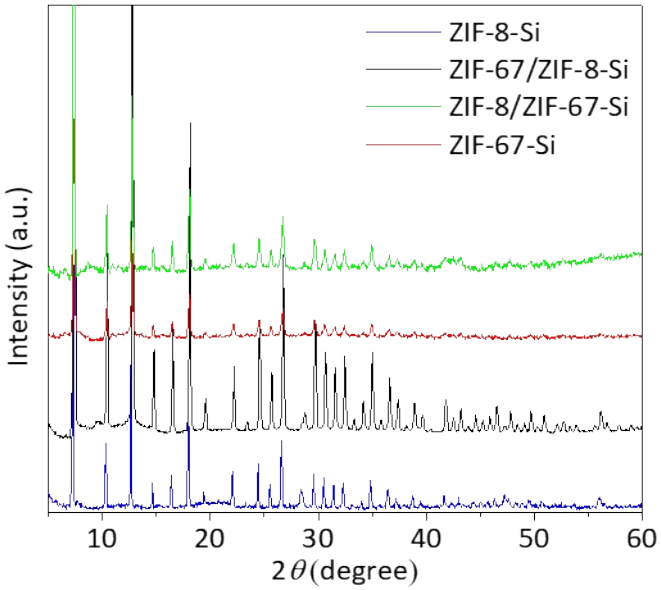

Fig. S2. XRD patterns of ZIF-Si samples. All observed peaks from the ZIF-Si samples can be assigned to ZIF-67, ZIF-8 and Si.

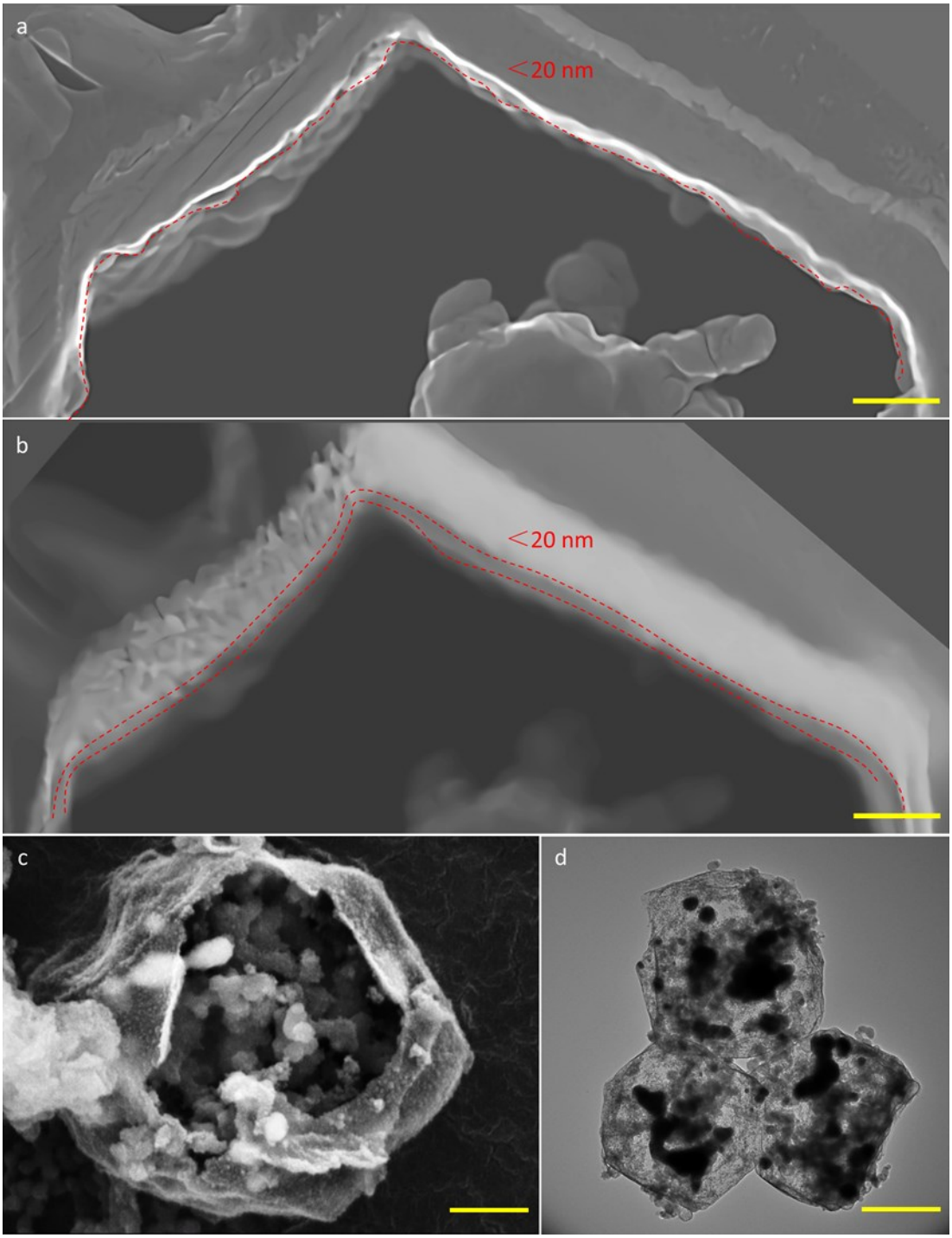

Fig. S3. Morphological and structural characteristics of Si/C. (**a**, **b**), Cross-sectional SEM and TEM images of Si/C shell (Scale bar: 100 nm). **c**, SEM image of a broken Si/C unit (Scale bar: 500 nm). **d**, Low magnification TEM image of Si/C (Scale bar: 500 nm).

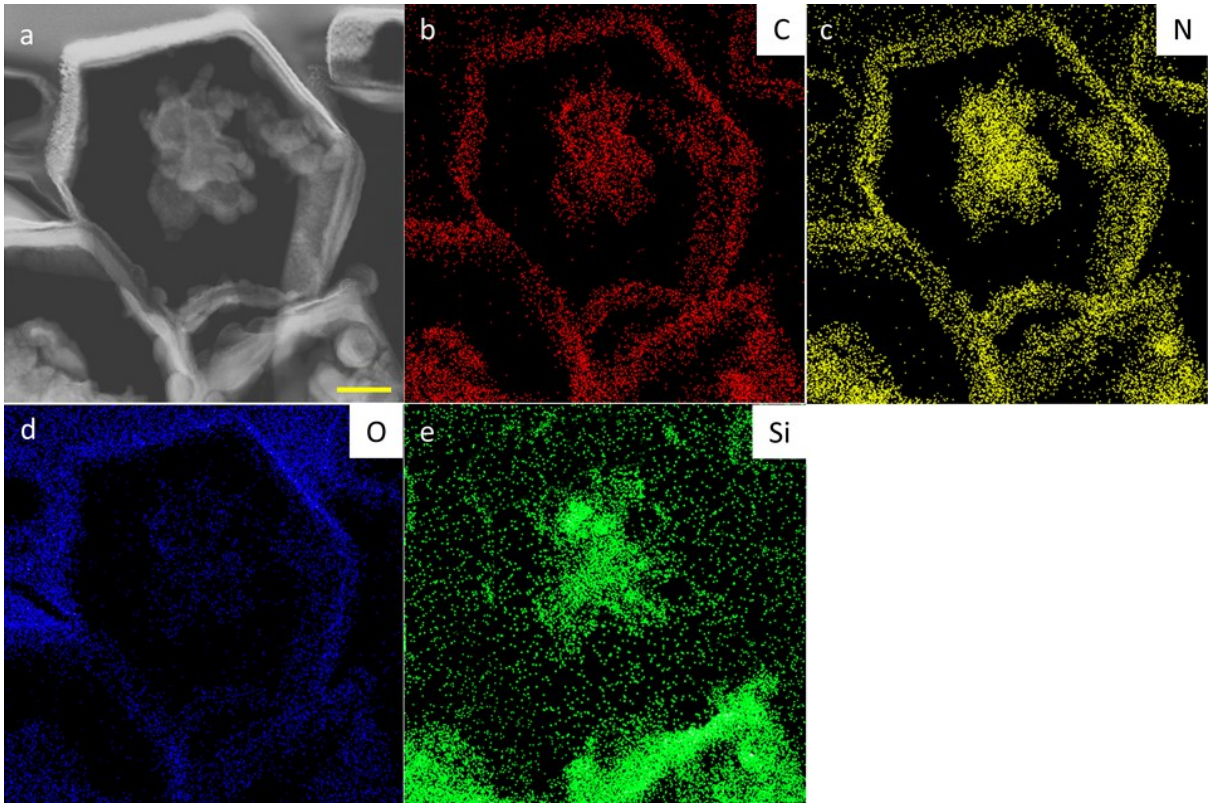

Fig. S4. a, TEM image of Si/C. (**b-e**), EDS mapping images of Si/C. Scale bar: 200 nm.

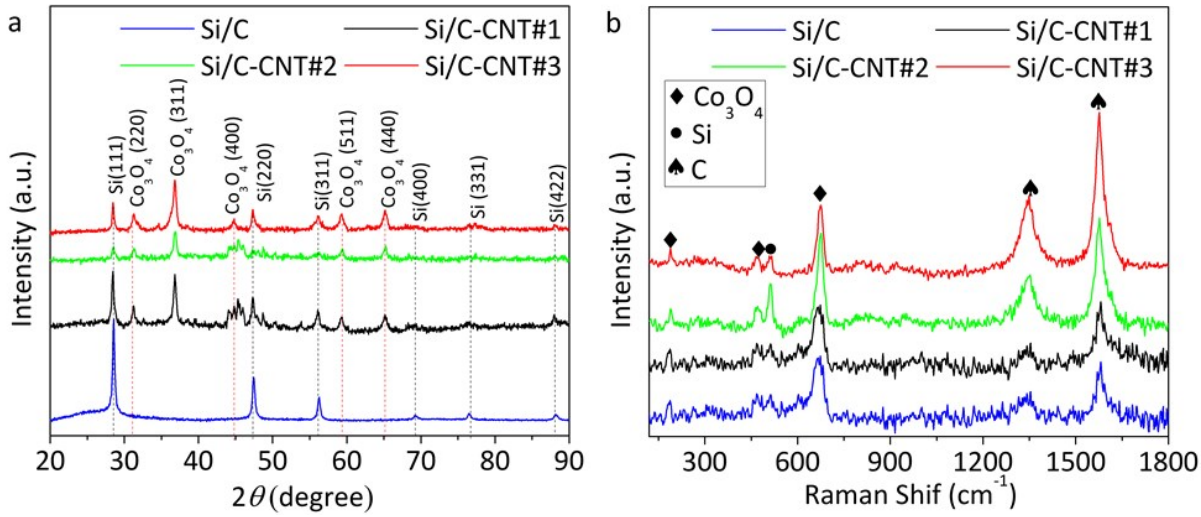

Fig. S5. a, XRD patterns of Si/C and Si/C-CNT samples. **b**, Raman spectra of Si/C and Si/C-CNT samples.

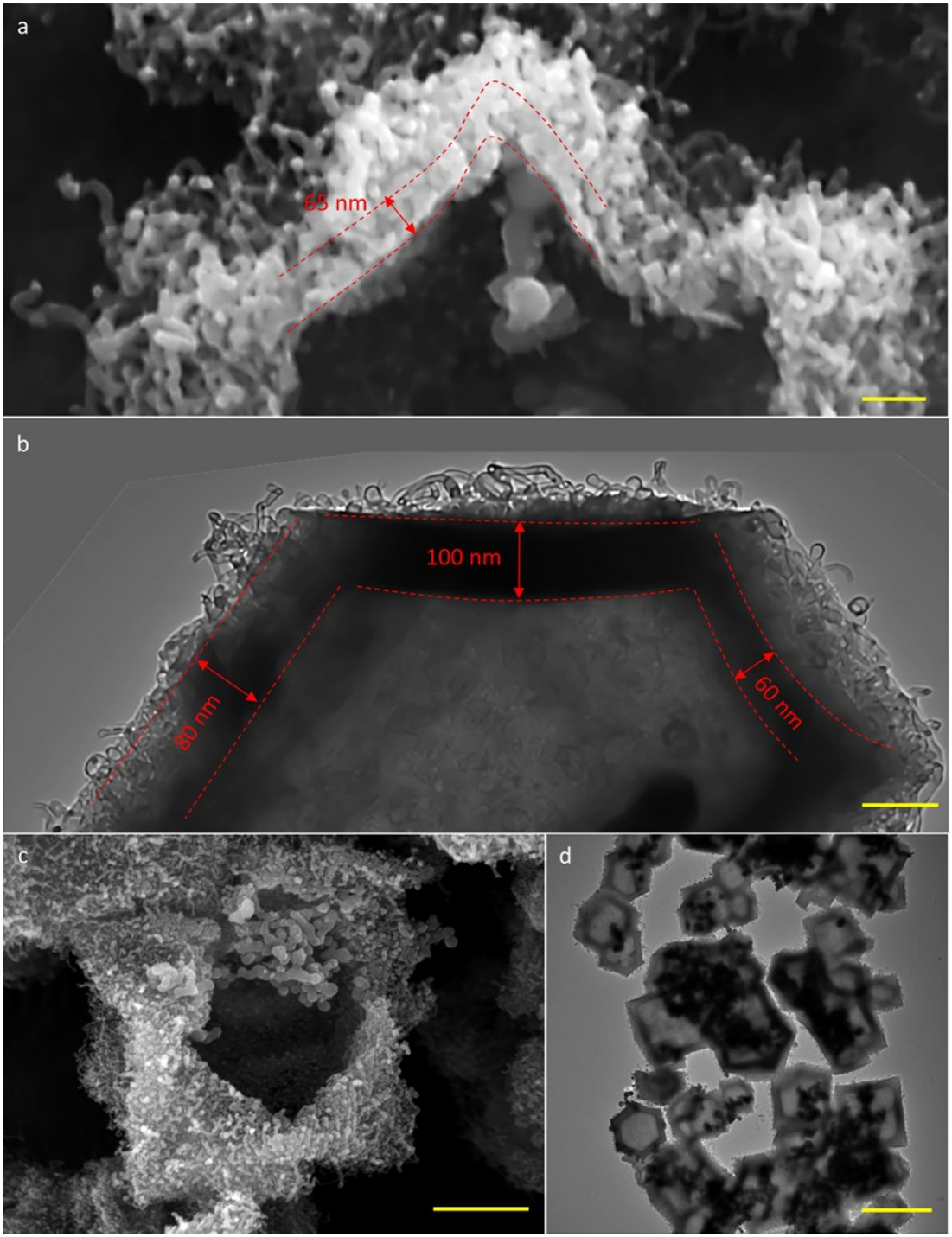

Fig. S6. Morphological and structural characteristics of Si/C-CNT#1. (**a**, **b**), Cross-sectional SEM and TEM images of Si/C-CNT#1 shell (Scale bar: 100 nm). **c**, SEM image of a broken Si/C-CNT#1 unit (Scale bar: 500 nm). **d**, Low magnification TEM image of Si/C-CNT-1 (Scale bar: 500 nm).

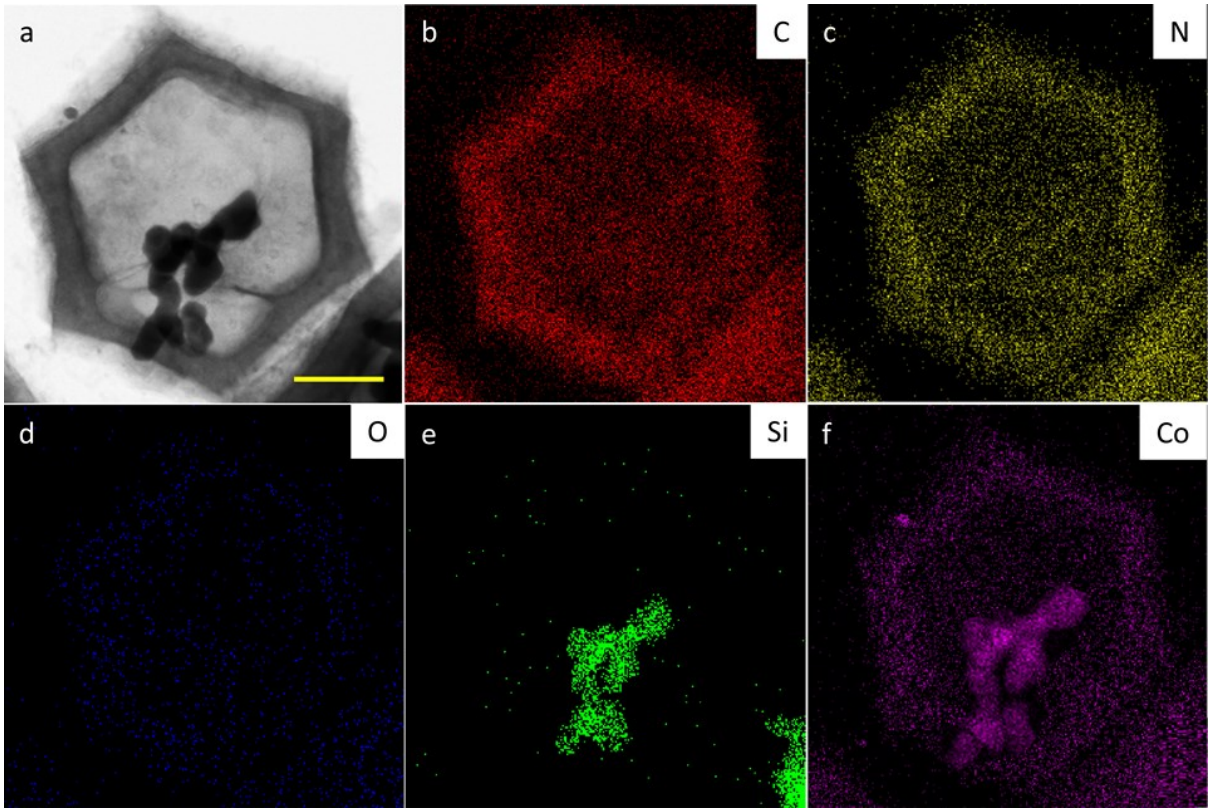

Fig. S7. a, TEM and (**b-f**), EDS mapping images of Si/C-CNT#1. Scale bar: 200 nm.

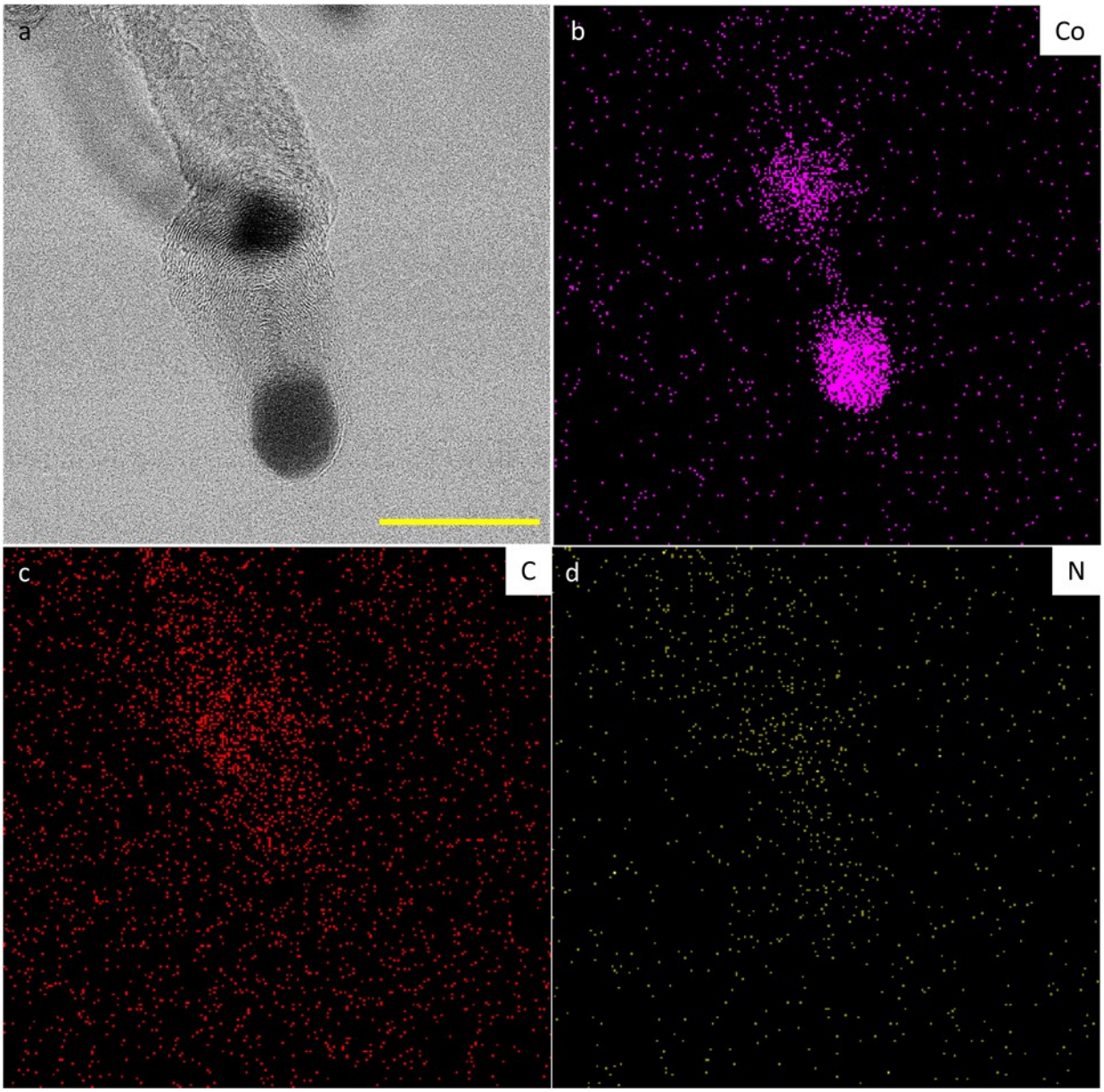

Fig. S8. a, HRTEM and (**b-d**), EDS mapping images of CNTs-Co_3O_4 NPs on the outer surface of Si/C-CNT#1. Scale bar: 20 nm.

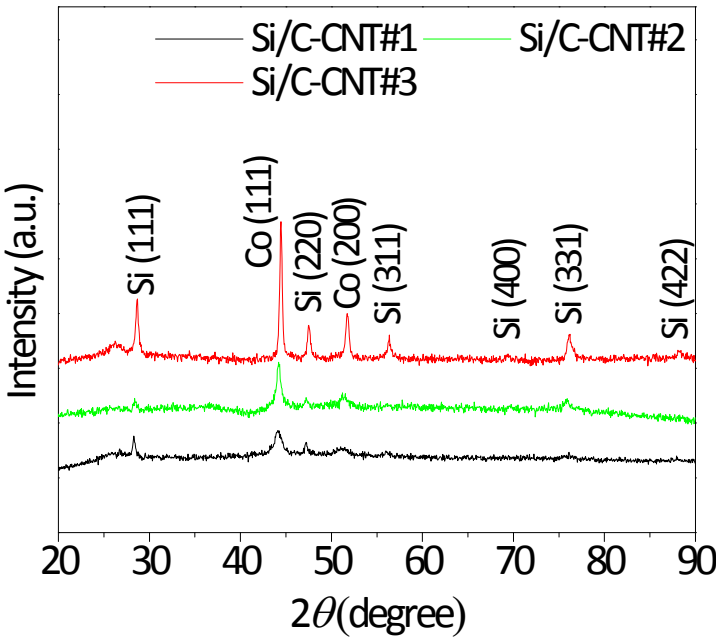

Fig. S9. XRD patterns of Si/C-CNT samples before air oxidation treatment.

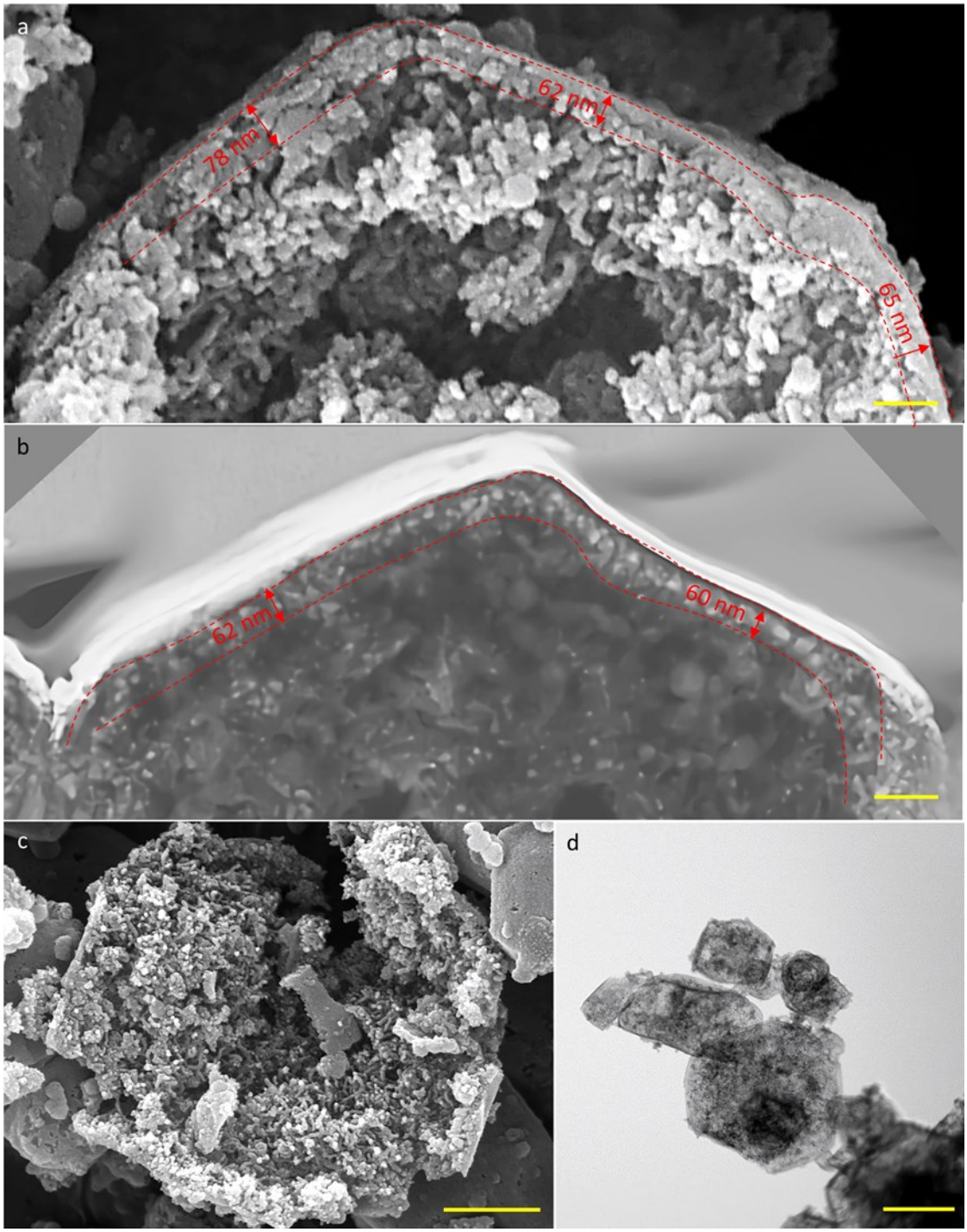

Fig. S10. Morphological and structural characteristics of Si/C-CNT#2. (**a**, **b**), Cross-sectional SEM and TEM images of Si/C-CNT#2 shell (Scale bar: 100 nm). **c**, SEM image of a broken Si/C-CNT#2 unit (Scale bar: 500 nm). **d**, Low magnification TEM image of Si/C-CNT-2 (Scale bar: 1 μm).

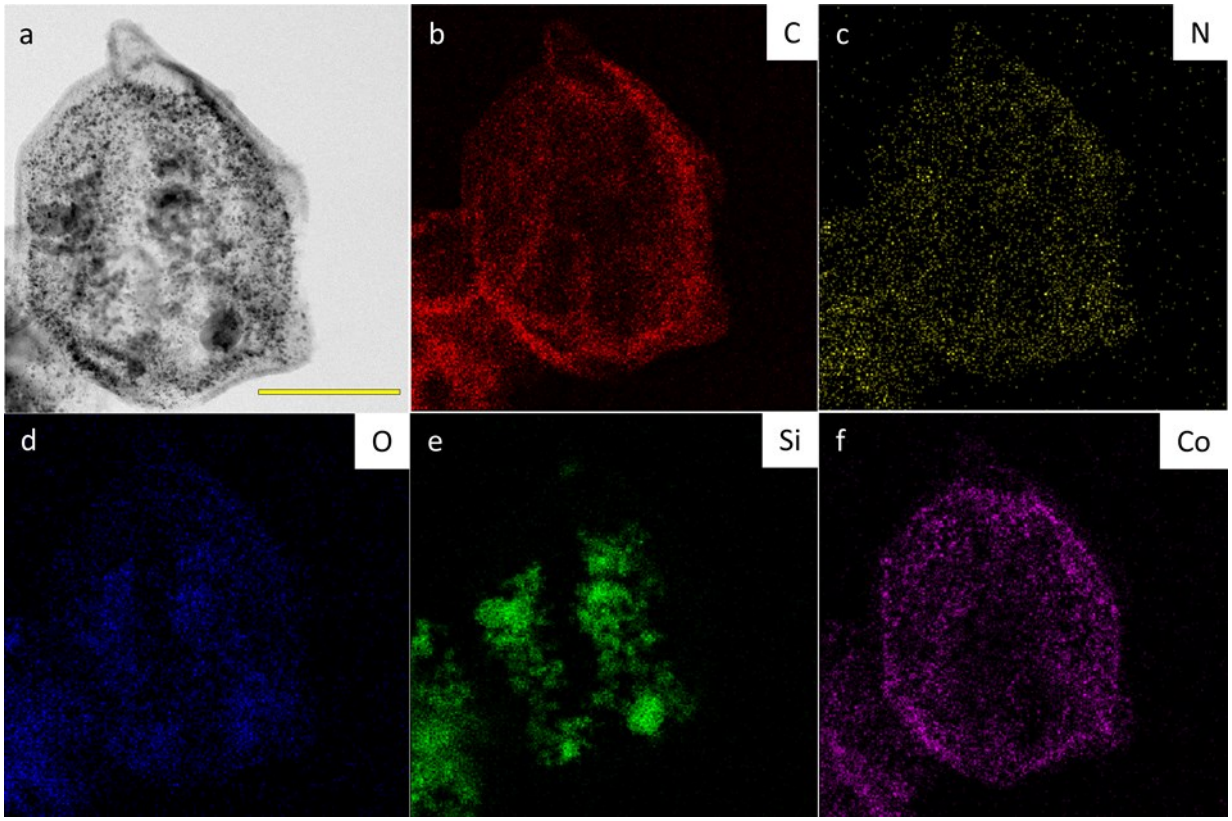

Fig. S11. a, TEM and (**b-f**), EDS mapping images of Si/C-CNT#2. Scale bar: 500 nm.

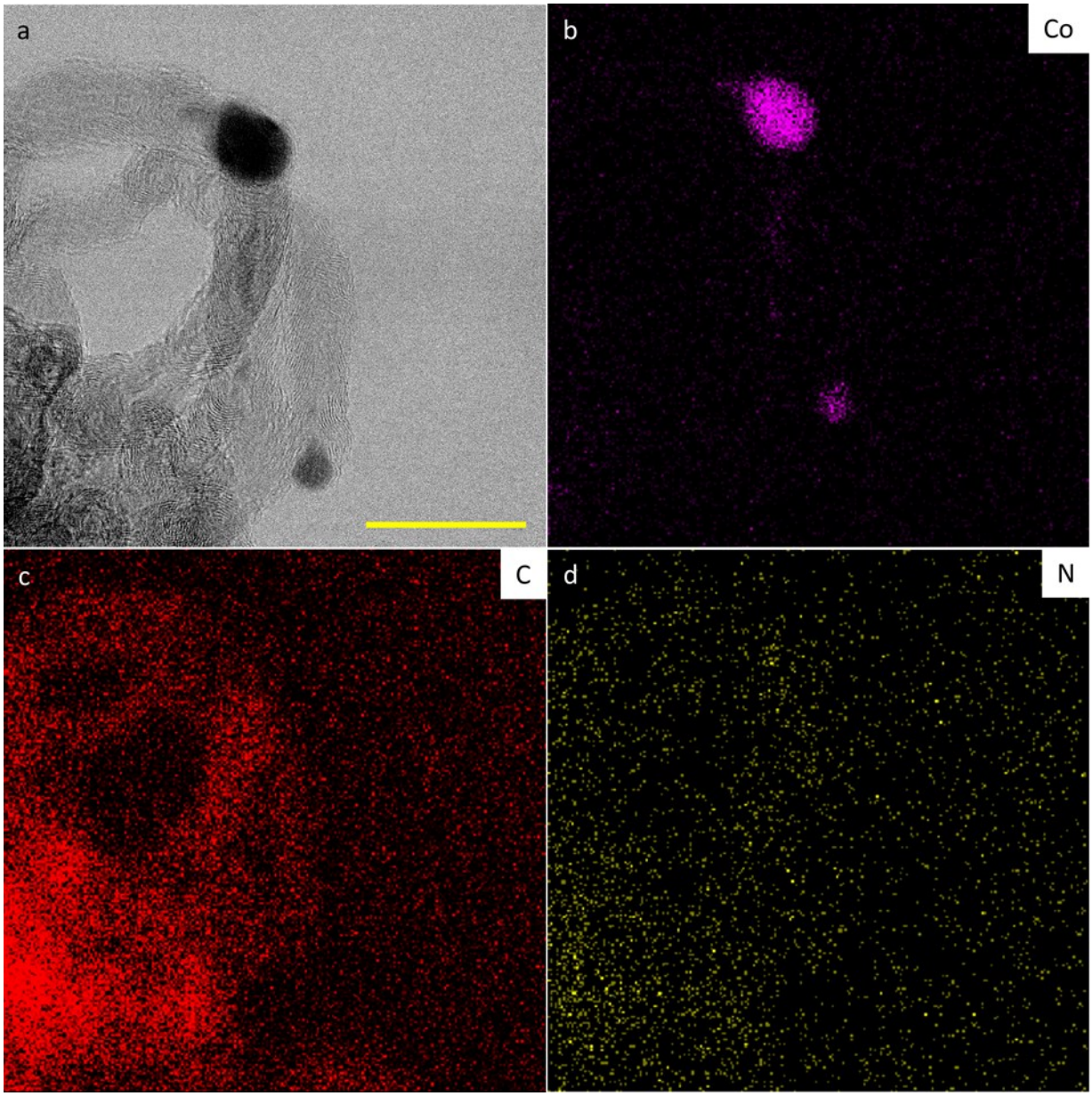

Fig. S12. a, HRTEM and (**b-d**), EDS mapping images of CNTs-Co_3O_4 NPs on the inner surface of Si/C-CNT#2. Scale bar: 20 nm.

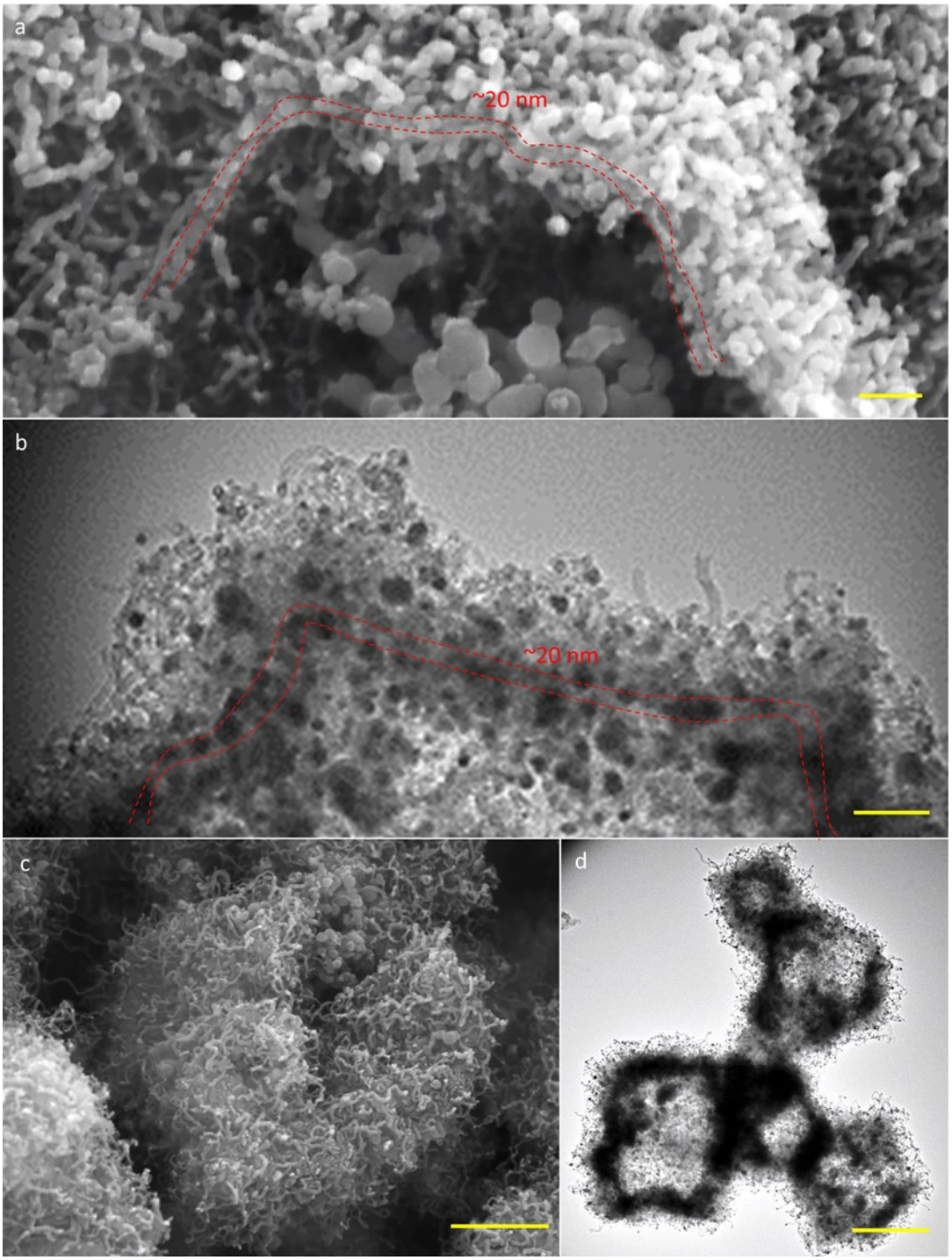

Fig. S13. Morphological and structural characteristics of Si/C-CNT#3. (**a**, **b**), Cross-sectional SEM and TEM images of Si/C-CNT#3 shell (Scale bar: 100 nm). **c**, SEM image of a broken Si/C-CNT#3 unit (Scale bar: 500 nm). **d**, Low magnification TEM image of Si/C-CNT-3 (Scale bar: 1 μm).

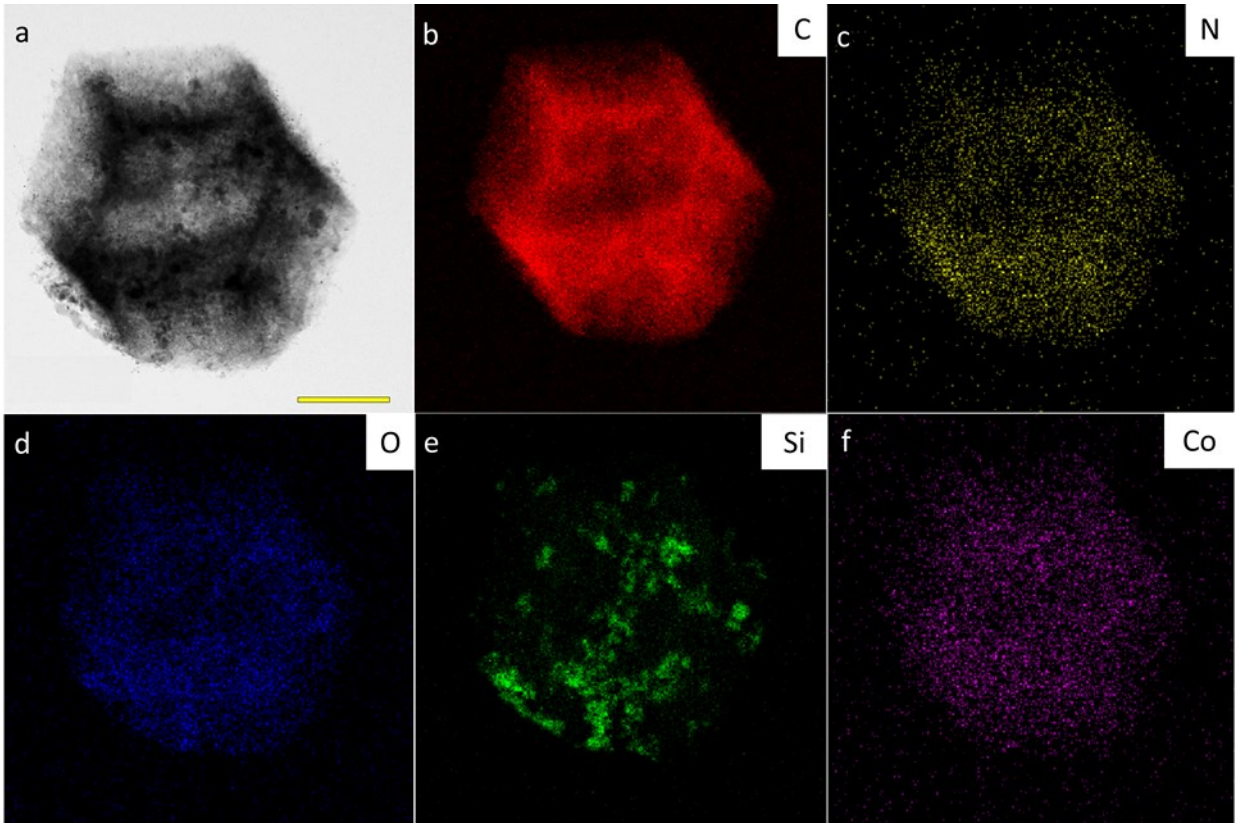

Fig. S14. a, TEM and (**b-f**), EDS mapping images of Si/C-CNT#3. Scale bar: 500 nm.

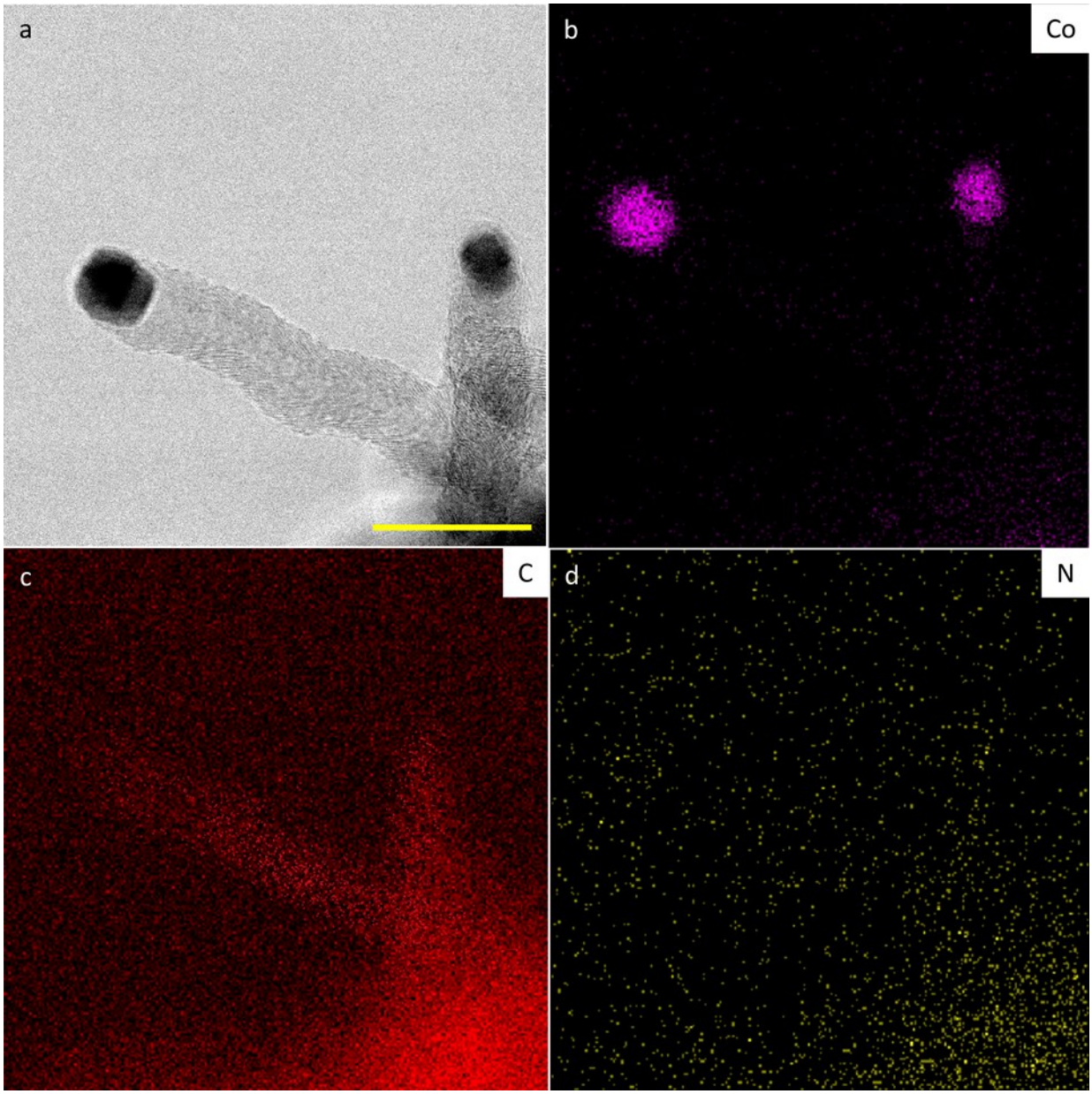

Fig. S15. a, HRTEM and (**b-d**), EDS mapping images of CNTs-Co_3O_4 NPs on the outer surface of Si/C-CNT#3. Scale bar: 20 nm.

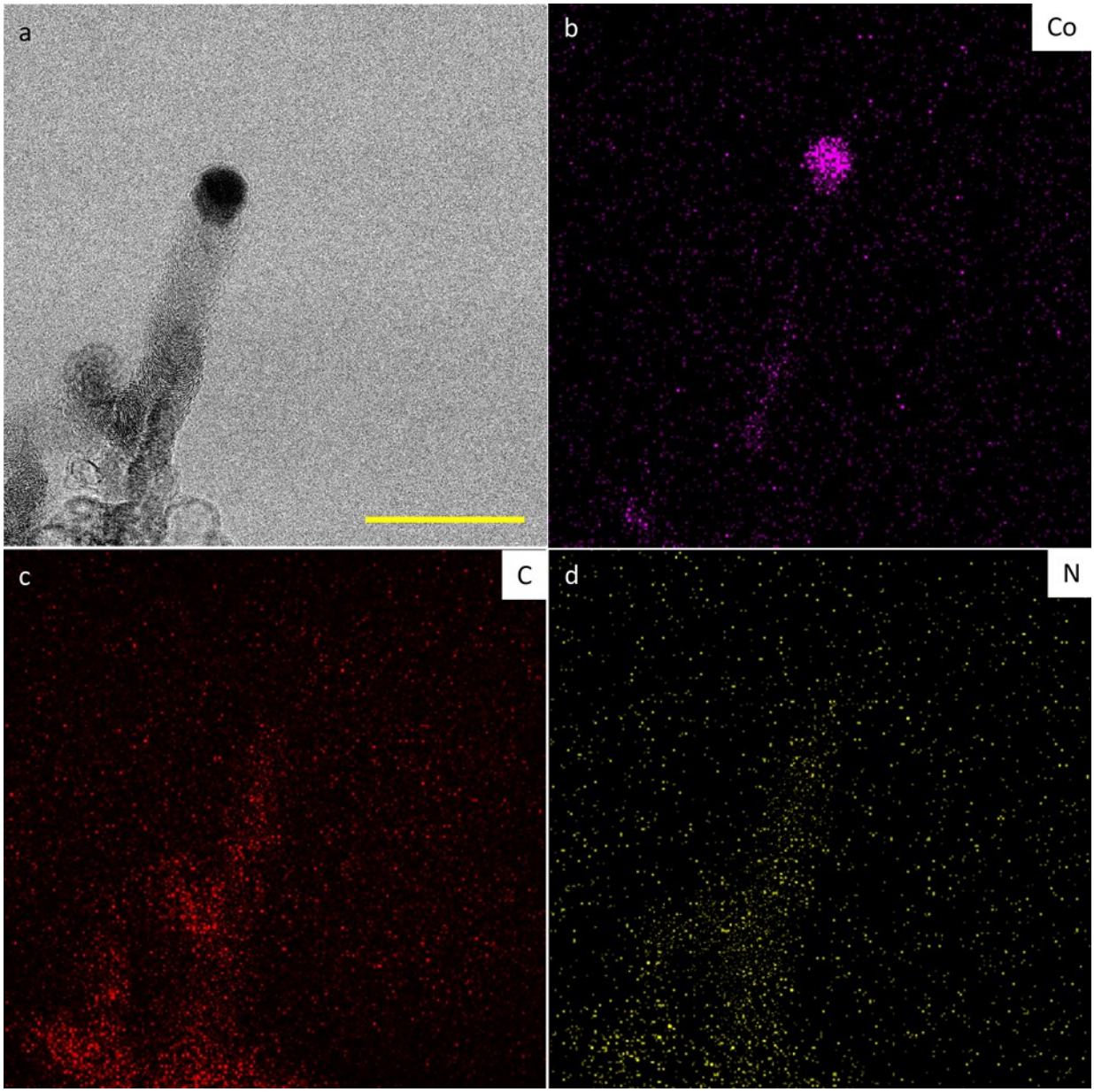

Fig. S16. HRTEM and (**b-d**), EDS mapping images of CNTs-Co_3O_4 NPs on the inner surface of Si/C-CNT#3. Scale bar: 20 nm.

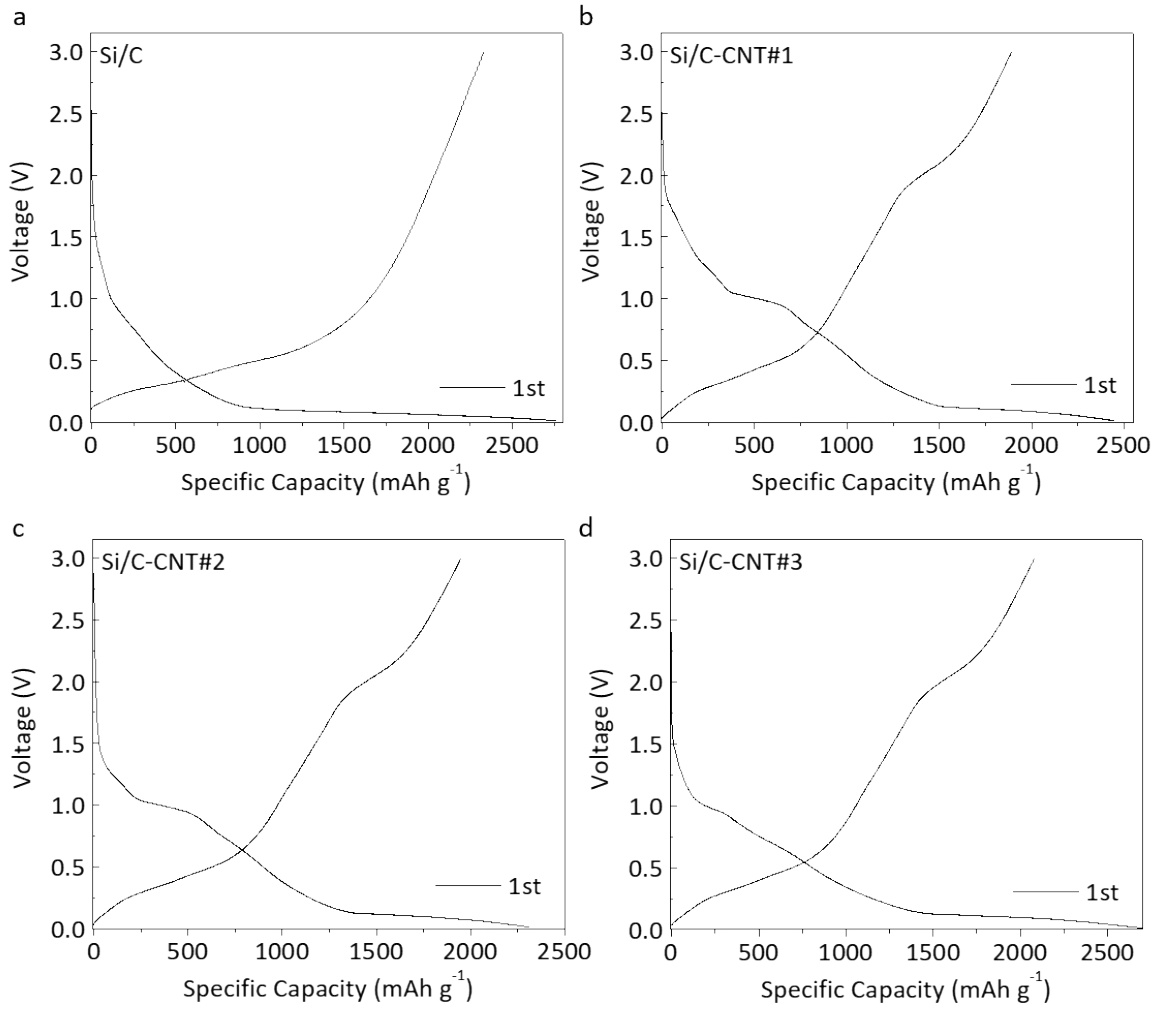

Fig. S17. Initial discharge-charge profiles of **a**, Si/C, **b**, Si/C-CNT#1, **c**, Si/C-CNT#2 and **d**, Si/C-CNT#3. Voltage range: 0.01 V–3.0 V. Current density: 0.1 A g^{-1}.

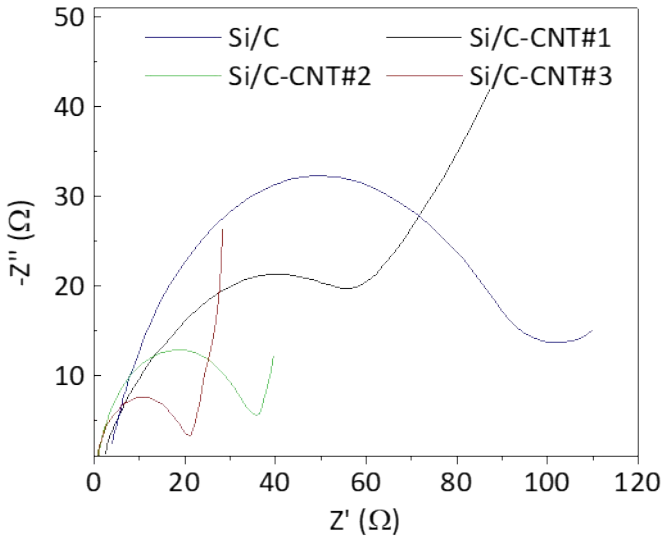

Fig. S18. Nyquist plots of Si/C and Si/C-CNT samples.

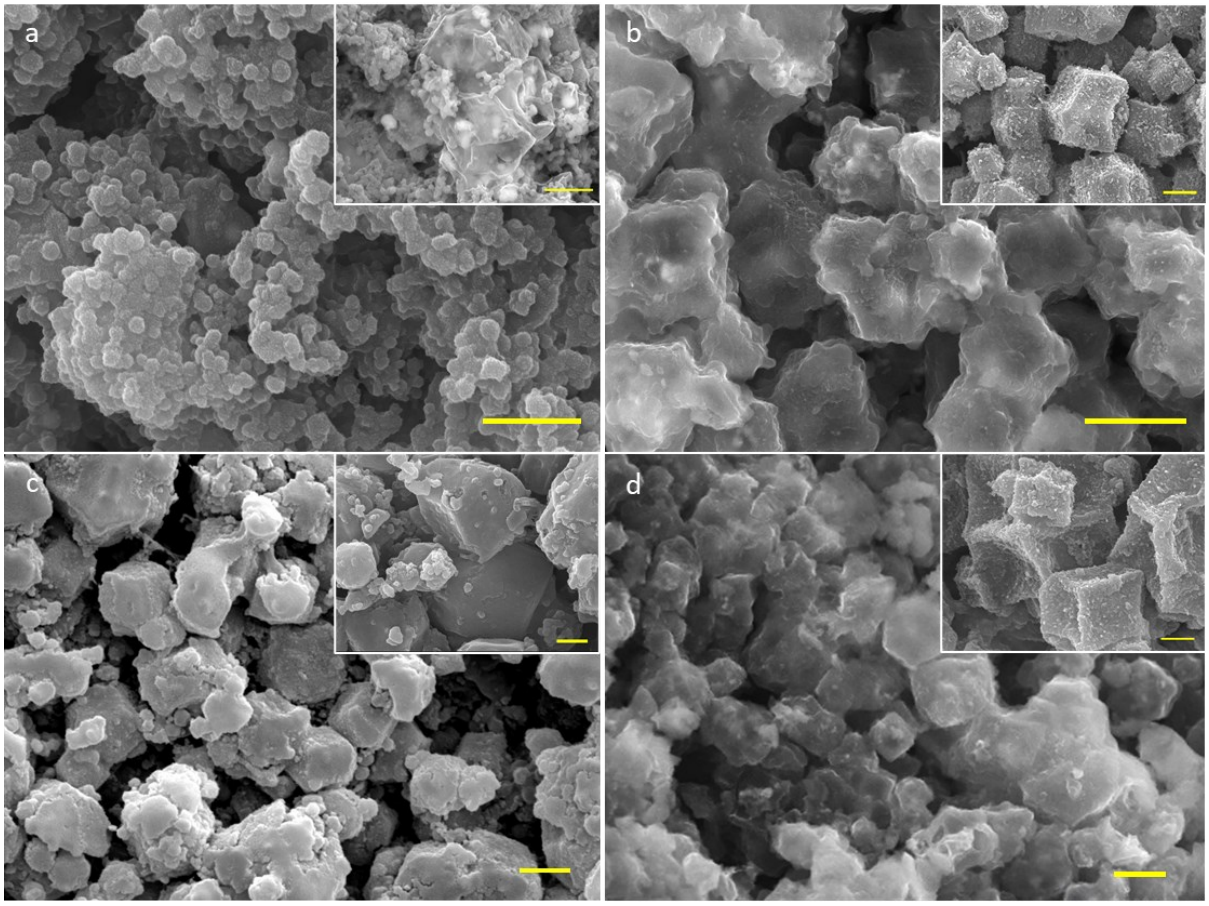

Fig. S19. SEM images of **a**, Si/C, **b**, Si/C-CNT#1, **c**, Si/C-CNT#2 and **d**, Si/C-CNT#3 after cycling test. Scale bar: 1 μm. Inserts are the SEM image of samples before cycling test. Scale bar: 500 nm.

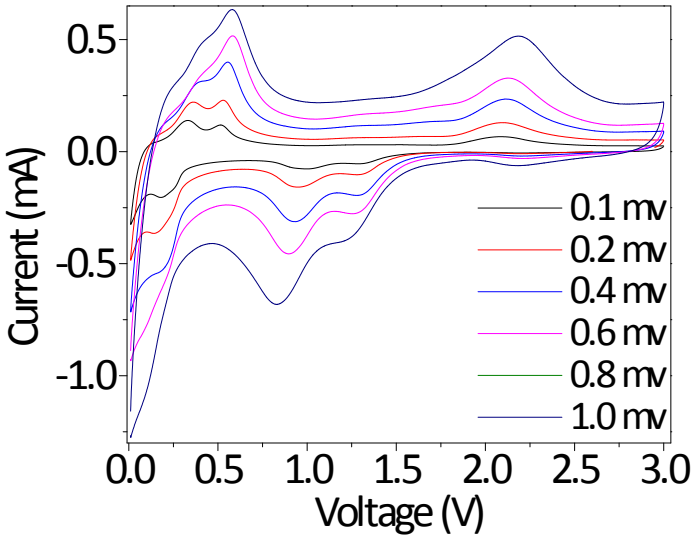

Fig. S20. CVs of Si/C-CNT#3 at different scan rates from 0.1 to 1.0 mV s^{-1} within a voltage range of 0.01–3.0 V.

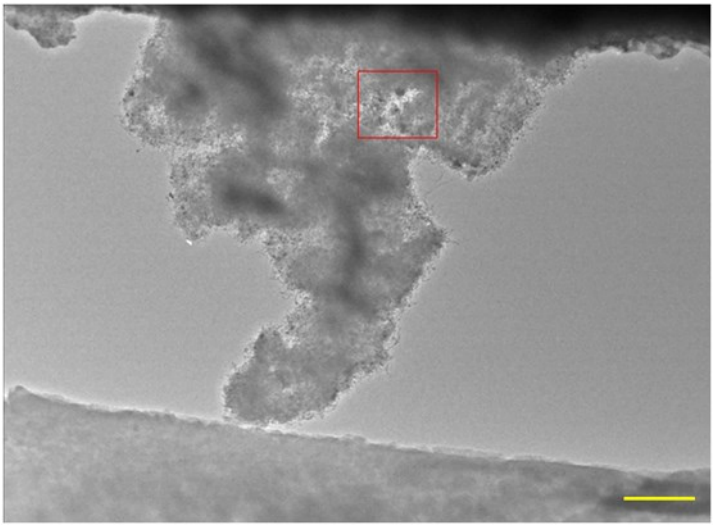

Fig. S21. In-operando recorded TEM image for a cluster of Si/C-CNT#3 units immobilised on the copper grid-working electrode. Red line enclosed area indicates the targeted set of Si NPs inside a Si/C-CNT#3 unit. Scale bar: 500 nm.

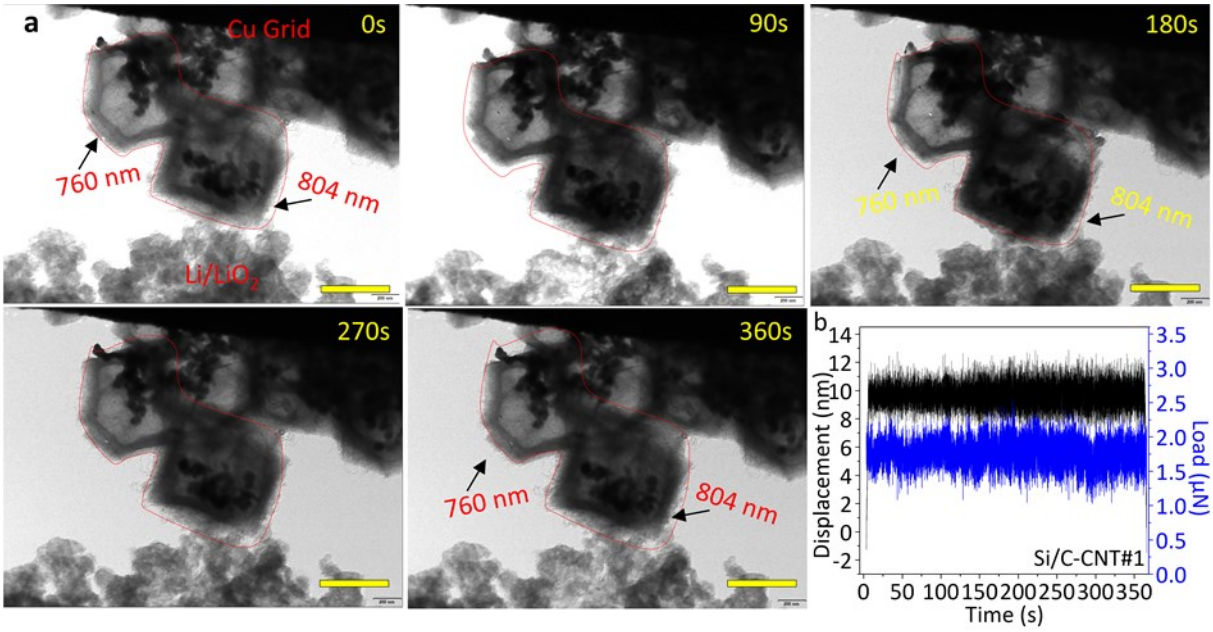

Fig. S22. a, Time-lapsed in-operando TEM images of the targeted cluster of Si/C-CNT#1 units during lithiation (0-180 s)/delithiation (180-360 s). **b**, Load- and displacement-time profiles during lithiation/delithiation. Scale bar: 500 nm.

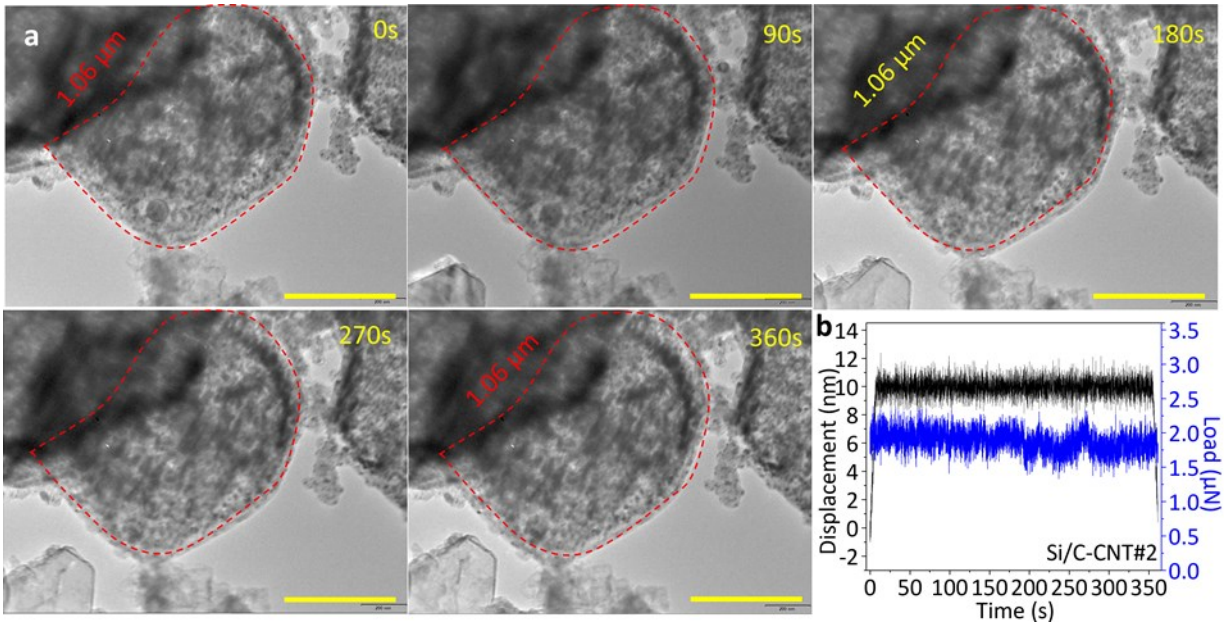

Fig. S23. a, Time-lapsed in-operando TEM images of the targeted cluster of Si/C-CNT#2 units during lithiation (0-180 s)/delithiation (180-360 s). **b**, Load- and displacement-time profiles during lithiation/delithiation. Scale bar: 500 nm.

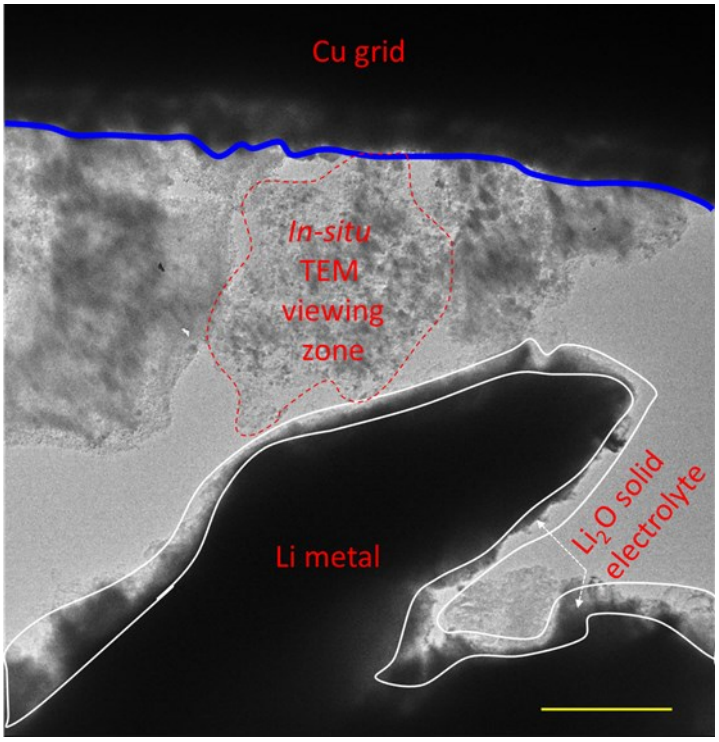

Fig. S24. Assembled TEM electrochemical measurement cell before inducing Li dendrite. Red line enclosed area shows the *in-situ* TEM viewing zone on a Si/C-CNT#3 structure unit. Scale bar: 1 μm.

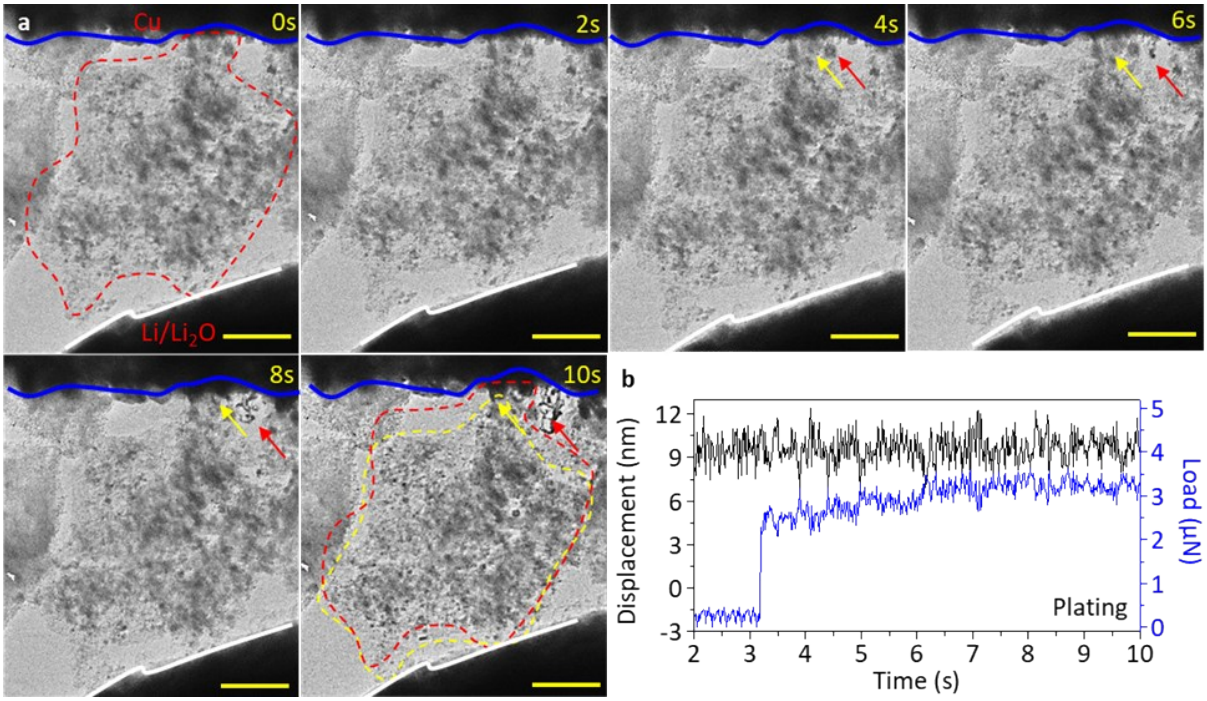

Fig. S25. a, Time-lapsed in-operando TEM images of Si/C-CNT#3 during the first 10 s of Li plating process. Scale bar: 500 nm. **b**, Corresponding load- and displacement-time profiles.

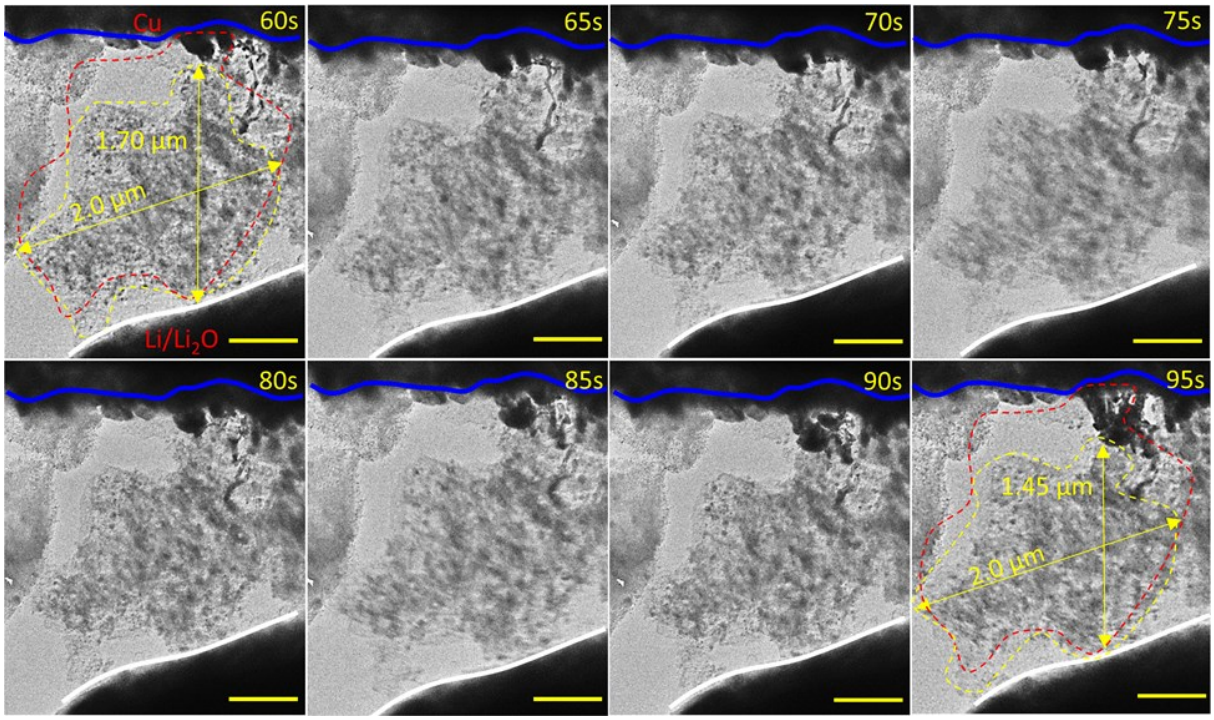

Fig. S26. Time-lapsed in-operando TEM images of the Si/C-CNT#3 during Li plating process between 60 and 95 s. Scale bar: 500 nm.

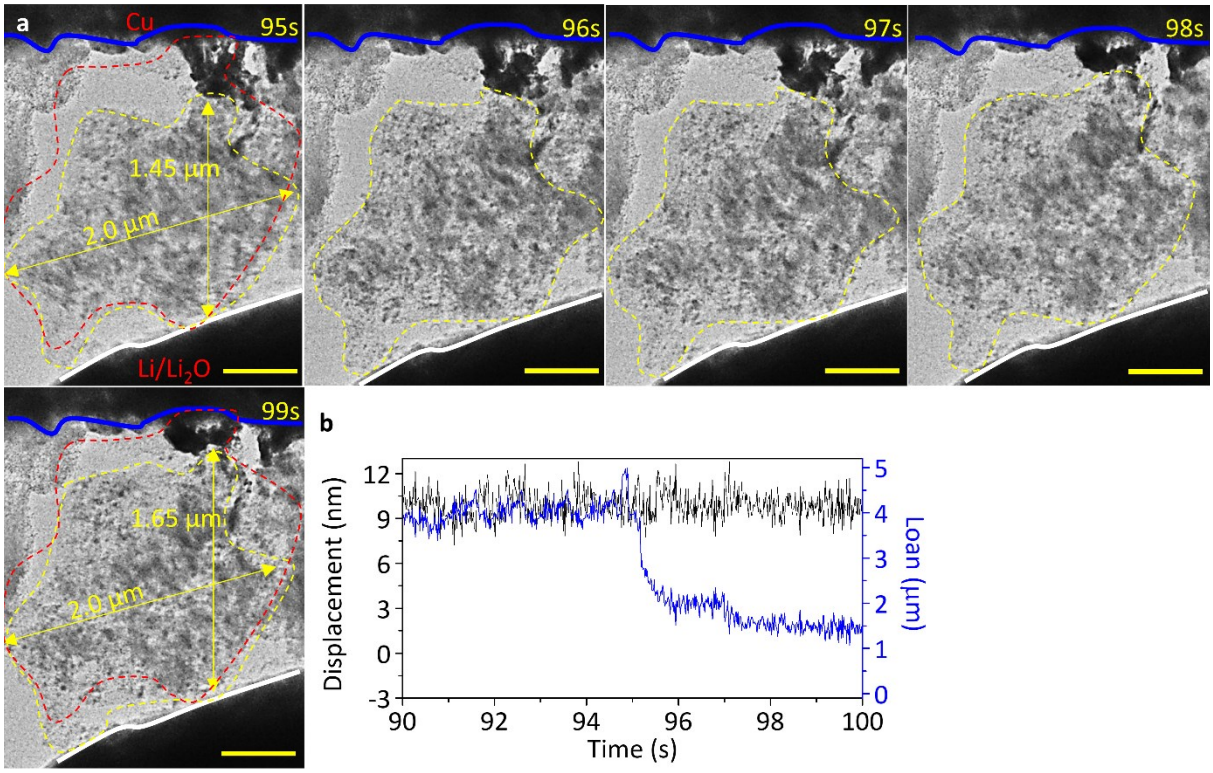

Fig. S27. a, Time-lapsed in-operando TEM images of the Si/C-CNT#3 during Li plating process between 95 and 99 s. Scale bar: 500 nm. **b**, Corresponding load- and displacement-time profiles.

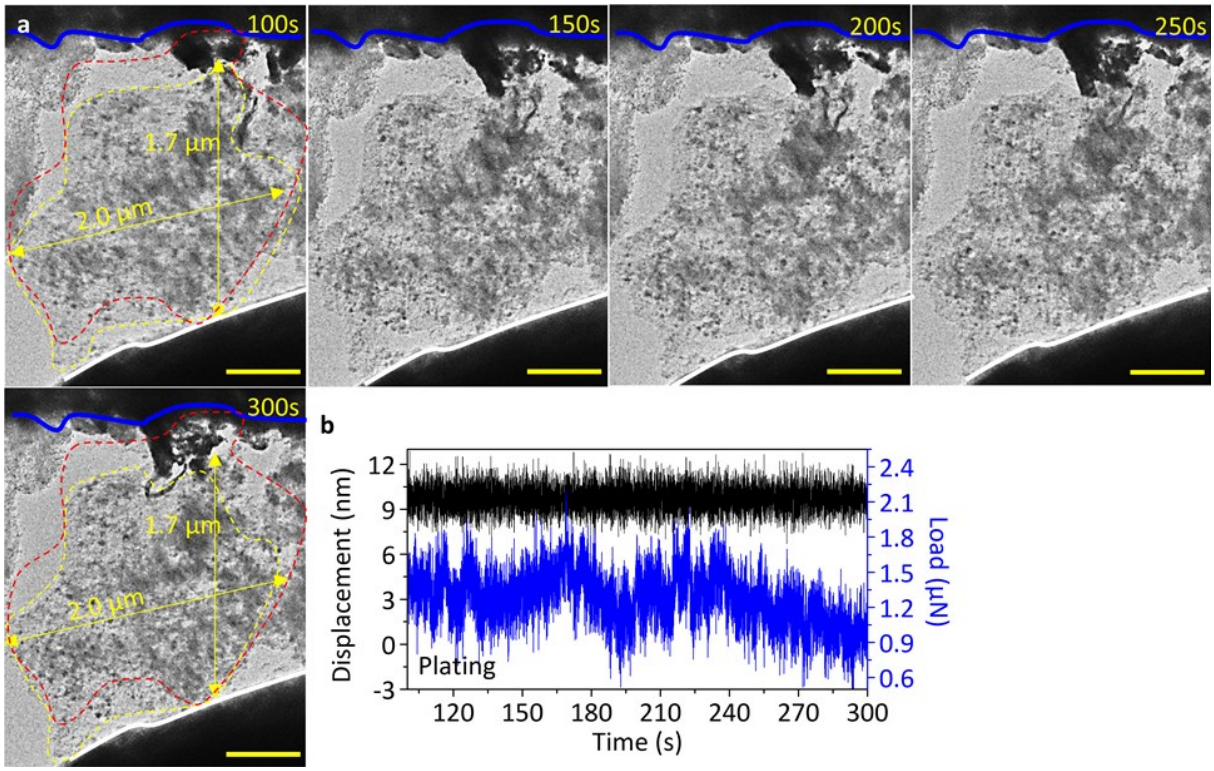

Fig. S28. a, Time-lapsed in-operando TEM images of the Si/C-CNT#3 during Li plating process between 100 and 300 s. Scale bar: 500 nm. **b**, Corresponding load- and displacement-time profiles.

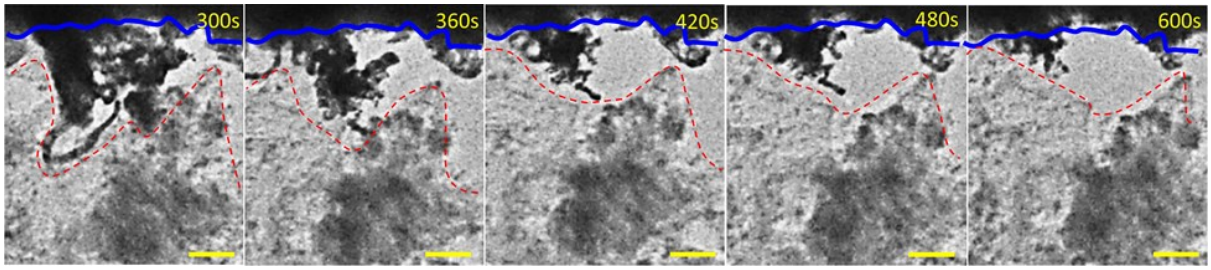

Fig. S29. Time-lapsed in-operando high magnification TEM images showing Li dendrites dissolution process. Scale bar: 100 nm.