ADVANCED
ENERGY
MATERIALS

Supporting Information

for *Adv. Energy Mater.,* DOI: 10.1002/aenm.202204075

Sequential and Dendrite-Free Li Plating on Cu Foil Enabled by an Ultrathin Yolk–Shell SiO_x/C@C Layer

Ruhan He, Yutao Wang, Chengyi Zhang, Zhenhui Liu, Pan He, Xufeng Hong, Ruohan Yu, Yan Zhao, Jingsong Wu, Liang Zhou, and Liqiang Mai**

·Supporting Information

Sequential and Dendrite-Free Li Plating on Cu Foil Enabled by an Ultrathin Yolk@Shell SiO_x/C@C Layer

Ruhan He, Yutao Wang, Chengyi Zhang, Zhenhui Liu, Pan He, Xufeng Hong, Ruohan Yu, Yan Zhao, Jingsong Wu, Liang Zhou*, Liqiang Mai*

Supplementary Figures: Figure S1-S21

Supplementary Videos: Videos S1

Materials and Method

1. Materials Synthesis

1.1 Synthesis of yolk-shell $SiO_x/C@C$

Yolk-shell $SiO_x/C@C$ spheres were prepared through a sacrificial-template method. Specifically, a mixed solution of ethanol (3 mL), water (47 mL), and concentrated ammonia aqueous solution (0.5 mL, 25 wt.%) was heated to 35 ^oC. 0.3 mL 3-thiocyanatopropyltriethoxysilane (TCPTES, 97%) was rapidly added under vigorous stirring and stirred at 35 ^oC for 8 h. Then, 0.8 mL vinyltriethoxysilane (VTES, 99%) was dropwise added into the above suspension. After reacting for 10 h, the double-layer organosilicon spheres were collected by centrifugation, washed with water and ethanol three times, and dried at 70 ^oC for 12 h. The white powders collected were re-dispersed in a solution containing 60 mL water and 4.5 mL ethanol and sonicated for 1 h. Then, 0.05625 mL pyrrole and 0.27 g ammonium persulfate (36 M aqueous solution) were added in turn and stirred for 12 h at 25 ^oC. The yolk-shell $SiO_x/C@C$ spheres were obtained after NaOH (2.0 M aqueous solution) etching at 60 ^oC for 6 h and annealing in N_2 at 800 ^oC for 3 h.

1.2 Synthesis of C shell

For the synthesis of the C shell, 150 mg polystyrene spheres were employed as hard templates and dispersed in a solution containing 60 mL water and 4.5 mL ethanol and sonicated for 1 h. Then, 0.05625 mL pyrrole, 0.27 g ammonium persulfate (36 M aqueous solution) were added in turn and stirred for 12 h at 25 ^oC. After that, the products were collected through and drying. At last, the derived powders were annealed in N_2 under 800 ^oC for 3 h.

2. Electrochemical measurements

$SiO_x/C@C$ decorated Cu electrode was prepared through a conventional doctor blade-casting method. Typically, $SiO_x/C@C$ powder and polyvinylidene fluoride (PVDF) binder with a mass ratio of 9:1 were dispersed in N-methyl-2-pyrrolidone

(NMP) in the absence of any conductive additives. The mixture was sonicated for 5 h and stirred for 12 h. The suspension was then cast onto a 5 μm thick copper foil and dried at 60 °C for 12 h. The electrode was cut into 12 mm circular disks with a total mass loading of ~0.5 mg/cm^2.

The LFP electrodes (LF0501) were purchased from Guangdong Canrd New Energy Technology Co. Ltd. The mass loading of active LFP was ~10.5 mg/cm^2.

For CE testing, either SiO_x/C@C decorated Cu, C shell decorated Cu or bare Cu foil was assembled into type 2016 coin cells with a separator (Celgard 2500) and Li metal as counter/reference electrode. For full cell testing, either SiO_x/C@C decorated Cu or bare Cu foil was paired with Li foil to electrochemically deposit Li metal. Afterward, the cells were disassembled and the electrodes with predeposited Li metal were paired with LFP electrodes. 1.0 M lithium bis-trifluoromethaesulphonylimide (LiTFSI) dissolved in 1, 3-dioxolane (DOL) and 1, 2-dimethoxyethane (DME) (1:1, volume ratio) with 2 wt.% lithium nitrate ($LiNO_3$) were used as electrolyte in battery testing. For half and full cells, 80 μL of electrolyte were used. The areal currents for lithium pre-deposition in half-cells and full-cells are both 1 mA cm^{-2}. For the pre-deposition of half-cell, lithium metal foil (anode) is paired with SiO_x/C@C-Cu electrode (cathode), and 3 mAh cm^{-2} of Li deposited on SiO_x/C@C-Cu electrode. For the pre-deposition of full-cell, lithium metal foil (anode) is paired with SiO_x/C@C-Cu electrode (cathode), and 3.2 mAh cm^{-2} of Li deposited on SiO_x/C@C-Cu electrode (N/P ratio = 2/1, areal capacity of LFP is 1.6 mAh cm^{-2}). All cell measurements were carried out using a LAND 8-channel battery tester.

3. Spectroscopic measurements

The spectroscopic measurements were obtained using a JEOL-7100F field emission SEM at 15 kV and a JEM-2100F TEM at 200 kV. STEM-EELS spectra were recorded with an FEI Titan Themis G2 60-300. *In-situ* TEM experiments were performed inside a TEM (FEI Talos F200s) using a TEM-STM (scanning tunneling microscope) *in-situ* sample holder (Zep Tools, China). Sectional SEM images were taken with the help of FIB (Focused ion beam) milling (FEI Helios Nanolab G3 UC) with a gallium ion source. XPS analysis was carried out on a Thermo ESCALAB 250XI. Thermogravimetric analysis was performed using a Netzsch STA 449 simultaneous analyzer. XRD pattern was collected on a Bruker D8 Advance X-ray diffractometer.

4. Computation methods

First principle simulations were carried out by the CASTEP module in the Materials Studio. The cut-off energy was set as 550 eV, the Γ-centered k-mesh was set as 3×3×3 for all calculations. The cell optimization was set as Full to fully release the stress in the structure. The convergence for max force, stress, and displacement were 0.01 eV/A, 0.03 GPa, and 0.001 Å, respectively. The Perdew-Burke-Ernzerh of generalized gradient approximation (GGA) and the ultrasoft pseudopotential for every atom were adopted.[1, 2]

The crystalline structures are constructed from the crystalline structure database and experimental results, while the amorphous structures were obtained by the quenching method with the ab initio molecular dynamics simulations. The system is firstly equilibrated at temperature 4000K at least for 5ps (5000 MD steps with a time step of 1fs), then quickly quenched to ~0 K and the lattice was fully relaxed.[3]

The adsorption energy (E_{adsor}) was calculated by the following equations:[4]

$$E_{adsor} = E_{total} - E_{sub} - E_{Li}$$

The E_{total}, E_{sub}, and E_{Li} indicates the energies of the complex system, the substrate, and Li-atom, respectively.

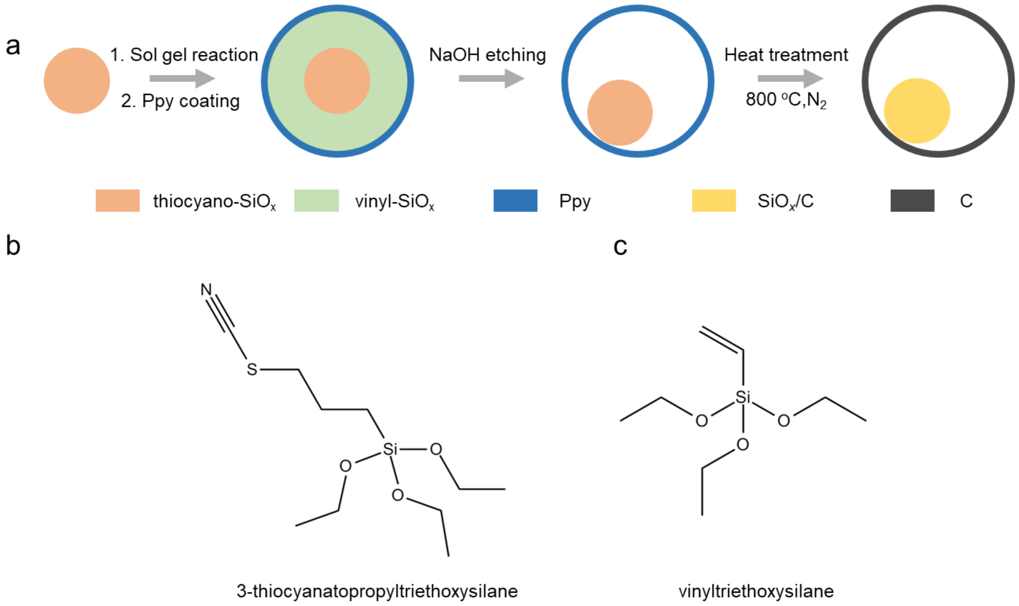

Figure S1. (a) The synthesis process of yolk@shell SiO_x/C@C. The molecular structure of (b) 3-thiocyanatopropyltriethoxysilane (TCPTES) and (c) vinyltriethoxysilane (VTES).

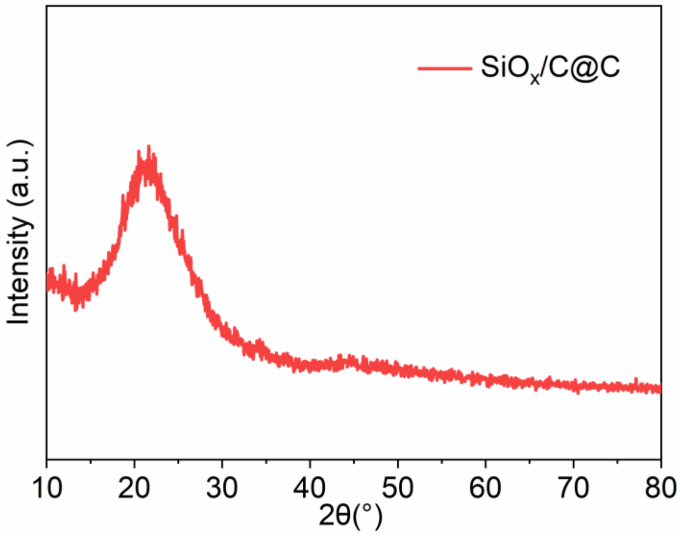

Figure S2. XRD pattern of SiO_x/C@C yolk-shell spheres.

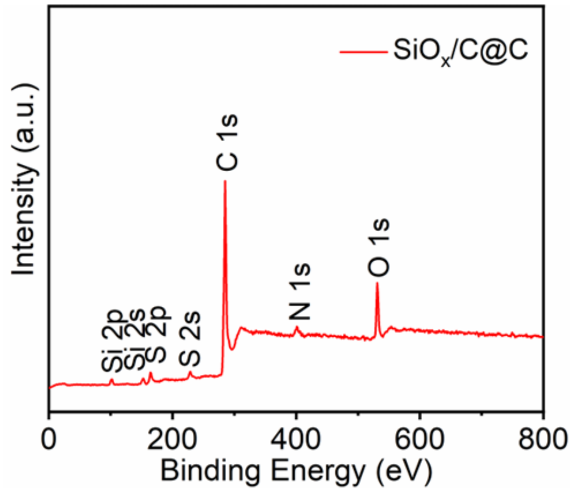

Figure S3. XPS survey spectrum of SiO$_x$/C@C yolk-shell spheres.

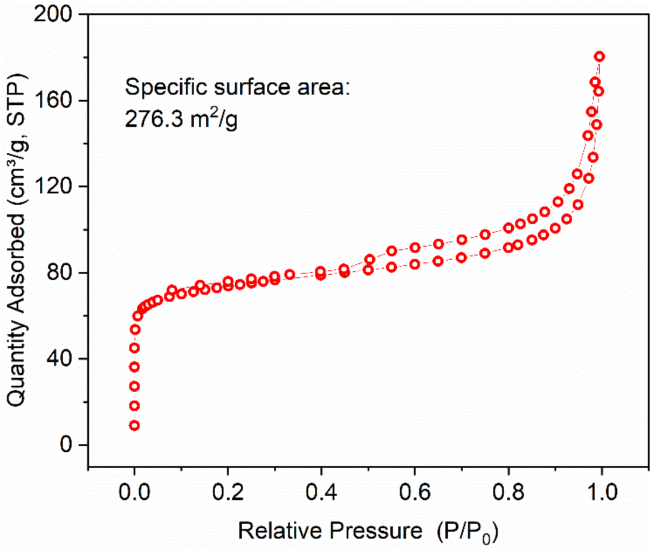

Figure S4. N_2 adsorption/desorption isotherms of SiO$_x$/C@C yolk-shell spheres.

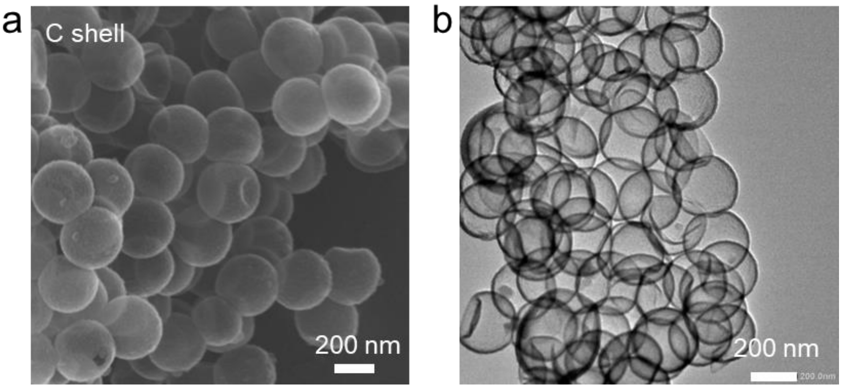

Figure S5. (a) SEM and (b) TEM images of C shells.

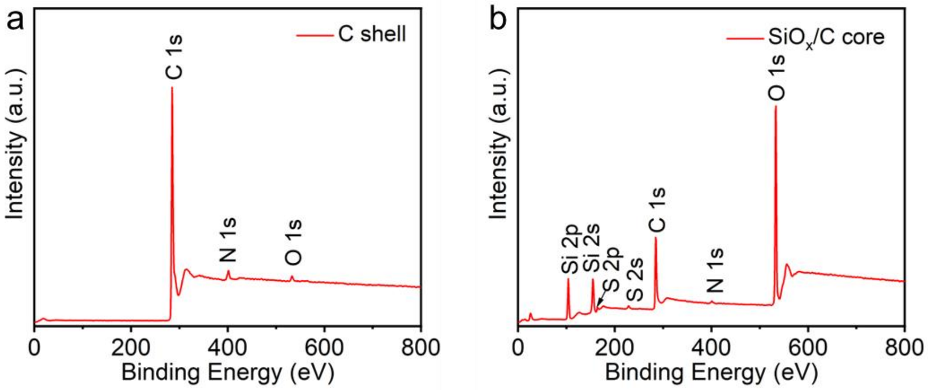

Figure S6. XPS survey spectra of (a) C shell and (b) SiO_x/C solid spheres.

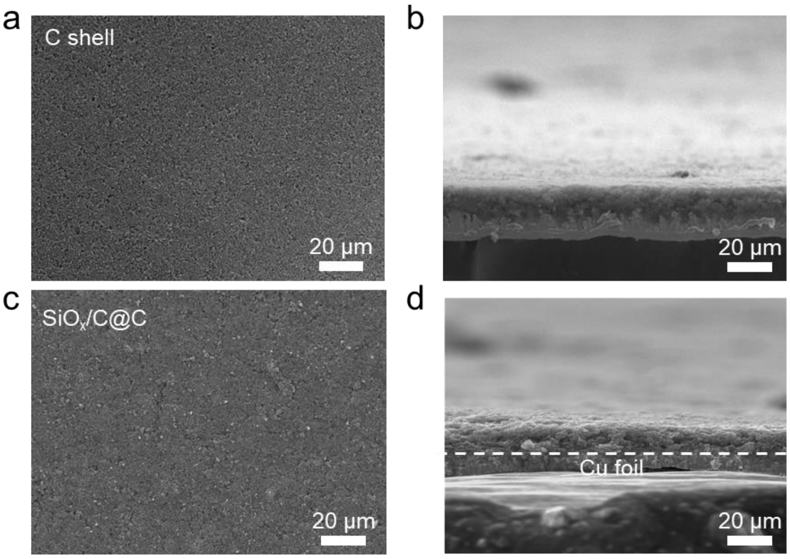

Figure S7. Plane view and cross-sectional SEM images of (a, b) C shell and (c, d) SiO$_x$/C@C decorated Cu foil.

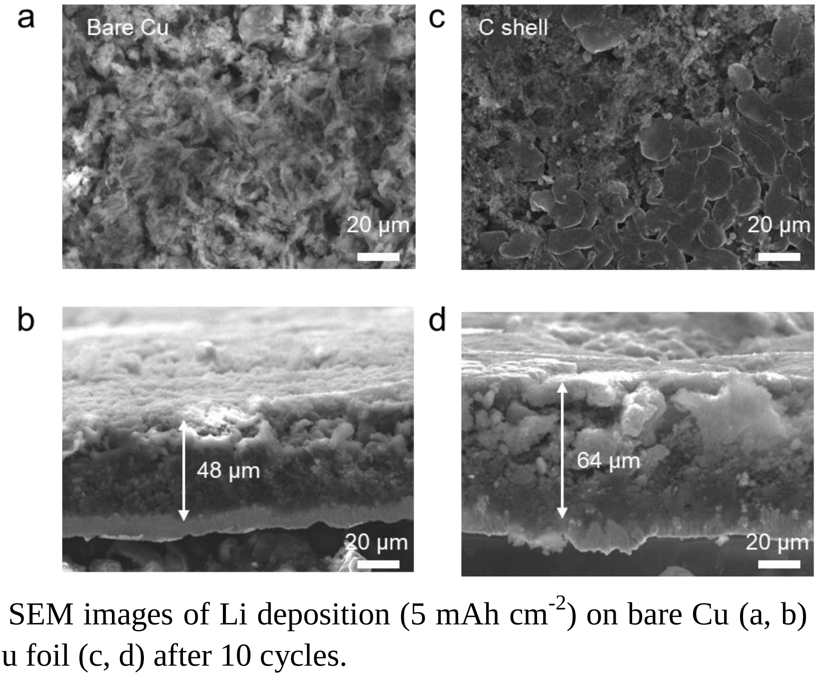

Figure S8. SEM images of Li deposition (5 mAh cm^{-2}) on bare Cu (a, b) and C shell modified Cu foil (c, d) after 10 cycles.

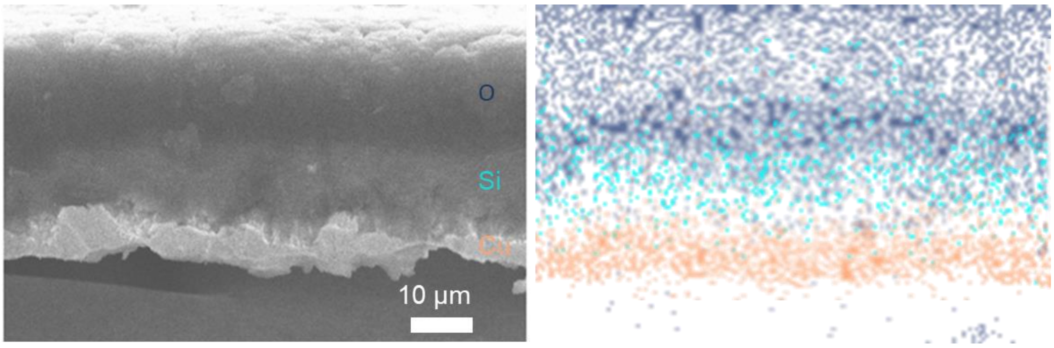

Figure S9. Cross-sectional view SEM image of Li deposited (5 mAh cm^{-2}) on SiO$_x$/C@C modified Cu at 1st cycle and the corresponding EDS elemental mapping of O, Si, and Cu.

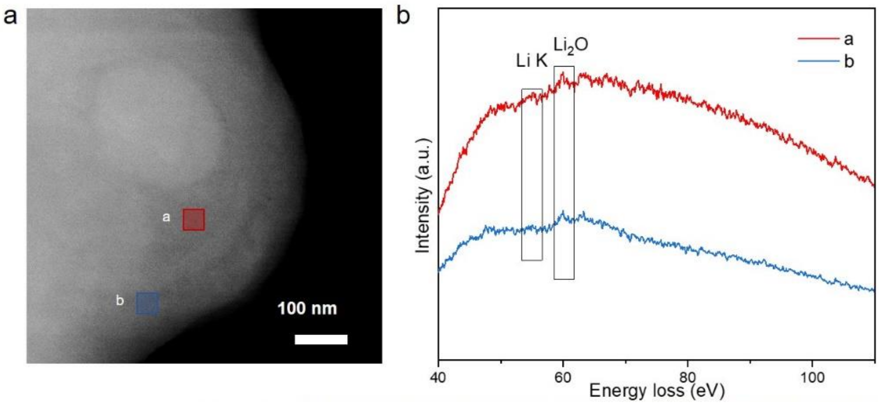

Figure S10. (a) HADDF-STEM image of SiO$_x$/C@C yolk-shell spheres with Li deposition in the interior void and (b) the corresponding EELS spectra of Li *K*-edge and Li$_2$O *K*-edge (point a: inside the void, point b: outside the void).

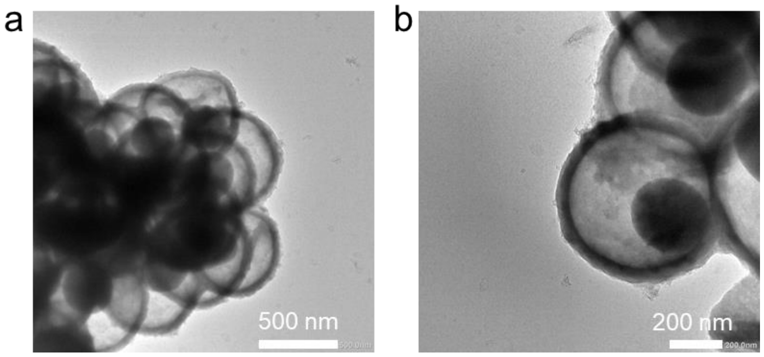

Figure S11. (a)-(b) TEM images of SiO_x/C@C yolk@shell spheres after 10 lithium plating/stripping cycles (5 mAh cm^{-2}).

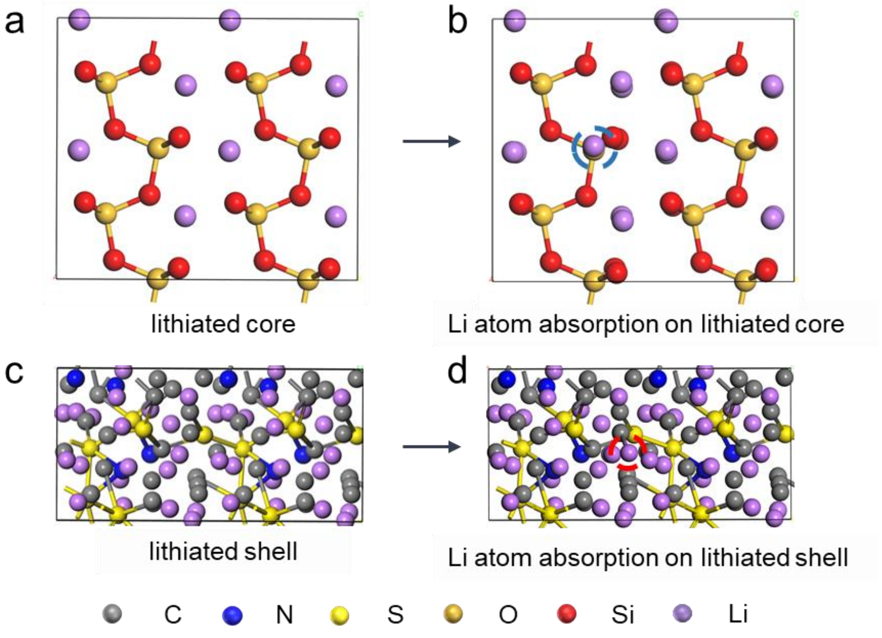

Figure S12. Molecular models of the (a) lithiated SiO_x/C core, (b) Li atom absorptoion on lithiated SiO_x/C core, (c) lithiated N/S co-doped C shell, (d) Li atom absorptoion on lithiated N/S co-doped C shell.

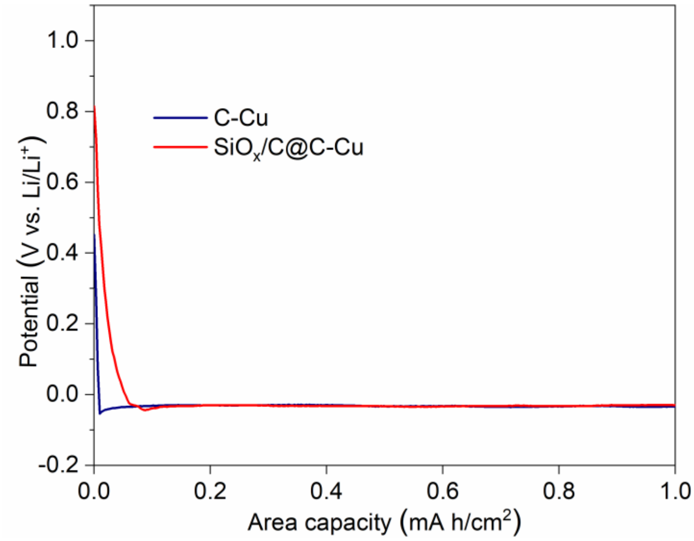

Figure S13. Discharge profiles of Li deposition on C decorated Cu foil and SiO$_x$/C@C decorated Cu foil (1 mA cm^{-2},1 mAh cm^{-2}).

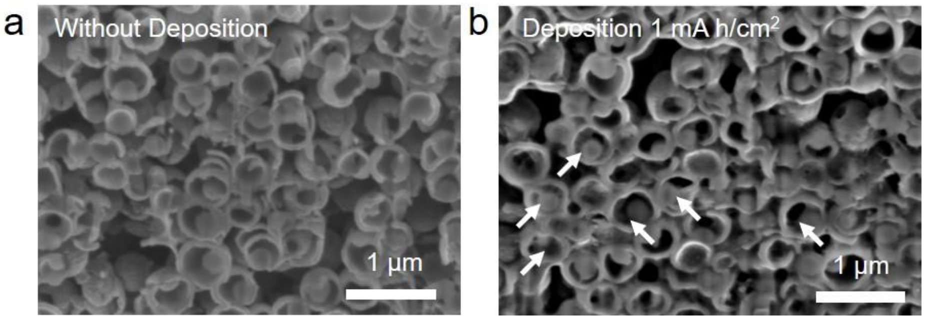

Figure S14. FIB cutting technique assisted cross-sectional SEM images of SiO$_x$/C@C decorated Cu foil (a) without Li deposition, (b) with Li plating mount of 1 mAh cm^{-2}.

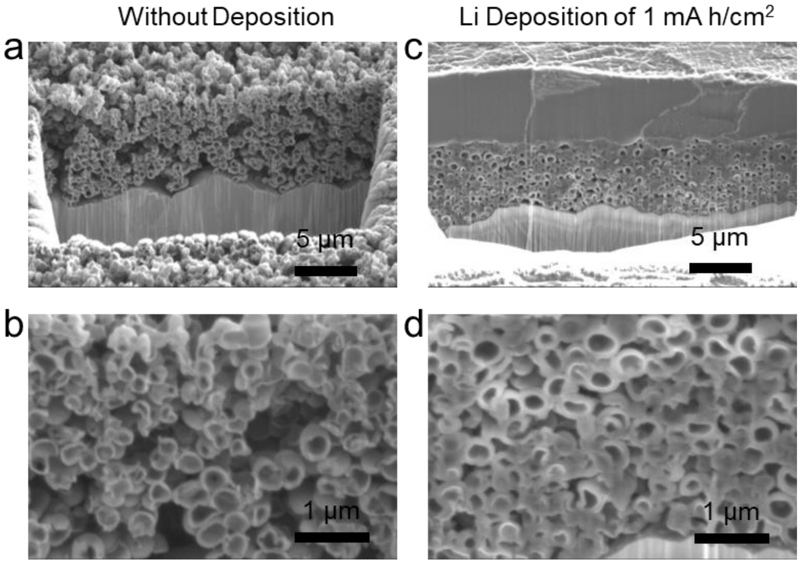

Figure S15. FIB cutting technique assisted cross-sectional SEM images of C shell decorated Cu foil (a-b) without Li deposition, (c-d) with Li plating mount of 1 mAh cm^{-2}.

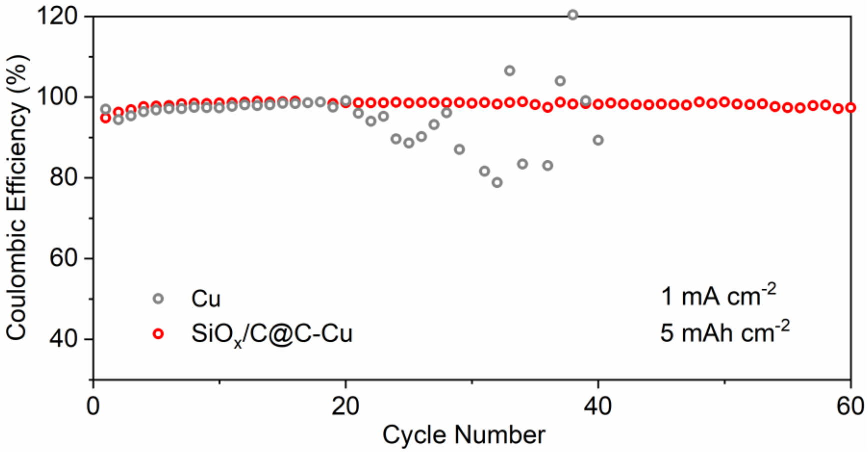

Figure S16. CE tests of bare Cu, C shell modified Cu, and SiO$_x$/C@C modified Cu (5 mAh cm^{-2}).

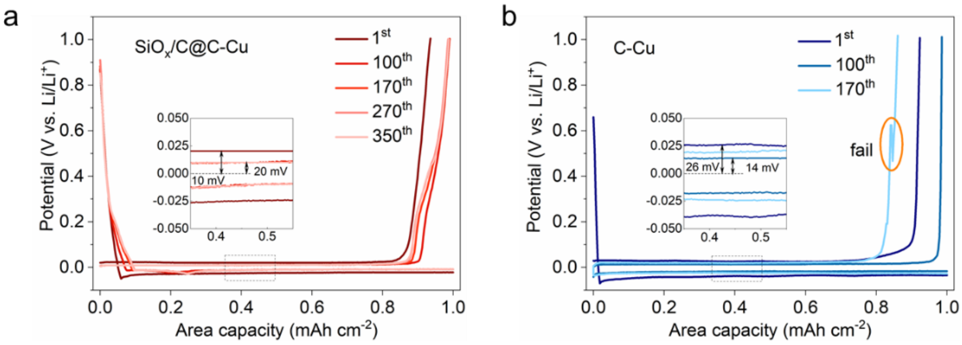

Figure S17. Discharge/charge profiles of CE tests for (a) Li-SiO$_x$/C@C-Cu electrode, (b) Li-C-Cu electrode.

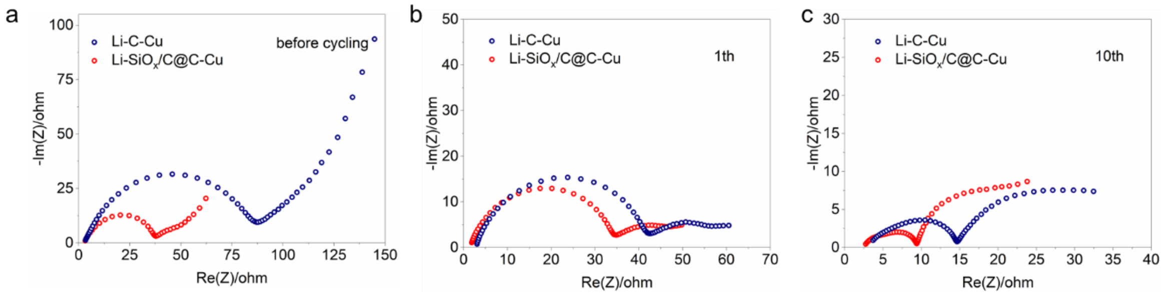

Figure S18. Impedance measurement of Li-C-Cu electrode and Li-SiO$_x$/C@C-Cu electrode (a) before cycling, (b) at the 1st cycle, and (c) at the 10th cycle.

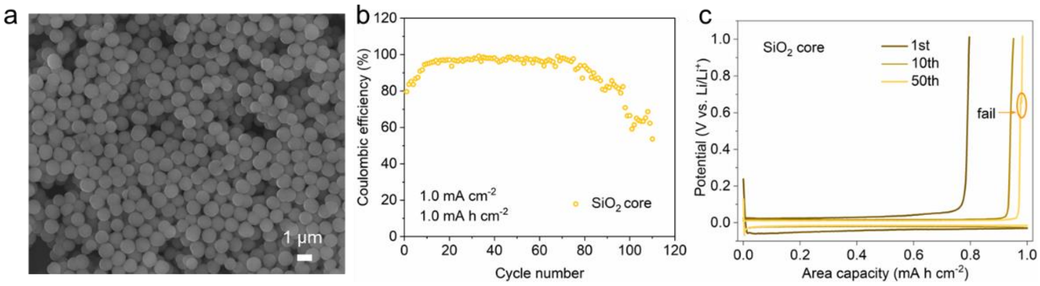

Figure S19. a) SEM images, b) CE tests, c) discharge/charge profiles from CE tests of SiO$_2$ core under 1.0 mA cm^{-2} and 1.0 mA h cm^{-2}.

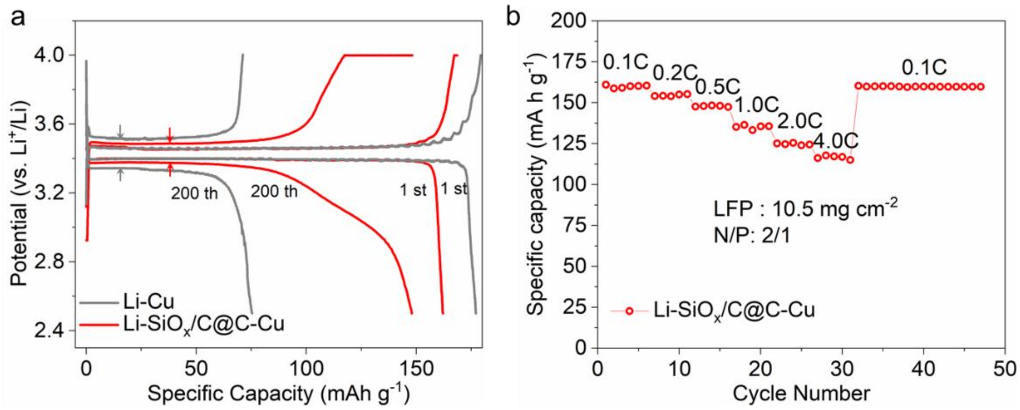

Figure S20. (a) Discharge/charge profiles of the Li-Cu||LFP and Li-SiO$_x$/C@C||LFP full cells at 1 C. (b) Rate performances at 0.1, 0.2, 0.5, 1.0, 2.0, and 4.0 C of the Li-SiO$_x$/C@C||LFP full cells.

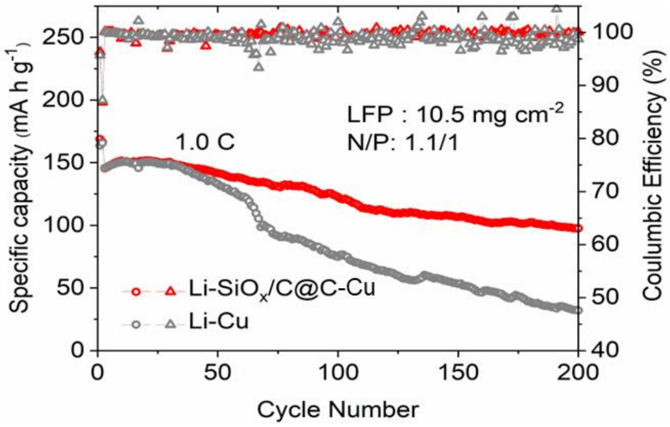

Figure S21. Cycling performances of the Li-Cu||LFP and Li-SiO$_x$/C@C-Cu||LFP full cells at charging/discharging rates of 1 C (1C = 170 mAh g^{-1}) with the N/P ratio of 1.1.

Table S1. The elemental analysis results of SiO_x/C@C yolk-shell spheres

Elements	N	S	C	H
Content ratio (wt%)	3.88	1.16	54.68	4.35

Table S2. Coulombic efficiency of Cu substrate modified with different materials as Li deposition substrates.

Substrates	Current density (mA cm^{-2})	Areal capacities (mAh cm^{-2})	Coulombic efficiency (%)	Cycle number	References
SiO_x/C@C-Cu	**1**	**1**	**98.5**	**400**	**This work**
	1	**2**	**98.6**	**200**	
Carbon shell + Au NP	0.5	1	98.0	300	Ref. [5]
Crumpled Graphene Ball	0.5	0.5	97.5	750	Ref. [6]
N-HPCSs	1	1	98.5	270	Ref. [7]
H-SiO_2/CNTs	0.2	1	99	200	Ref. [8]
WGC	1	1	97	100	Ref. [9]
CNT@SiO_x–C	1	1	98	200	Ref. [10]
MPTS-Cu	0.5	1	98.7	100	Ref. [11]
	1.5	1	96.0	100	
CLCS	1	2	97.3	700	Ref. [12]

The Coulombic efficiency of the half-cells referred in this table are all tested using the 1 M LiTFSI in DOL/DME-based electrolyte.

Table S3. Full cell cycling test of Cu substrate modified with different materials as Li deposition substrates (paired with $LiFePO_4$, LFP).

Substrates	Current density	Mass loading of LFP (mg cm^{-2})	N/P ratio	Specific capacity (mAh g^{-1})	Cycle number	References
SiO_x/C@C-Cu	**1C**	**10.5**	**2**	**140**	**350**	**This work**
N-HPCSs	0.2C	5	n/a	141	200	Ref. [7]
H-SiO_2/CNTs	0.5C	n/a	2.8	~140	50	Ref. [8]
WGC	0.5C	9	> 2	120	340	Ref. [9]
Hollow carbo sphere-modified electrode	1 mA cm^{-2}	n/a	n/a	135	40	Ref. [13]

The Coulombic efficiency of the half-cells referred in this table are all tested using the 1 M LiTFSI in DOL/DME-based electrolyte or high concentrated electrolyte. (1C = 170 mAh g^{-1})

References

[1] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.

[2] D. Vanderbilt, *Phys. Rev. B* **1990**, *41*, 7892.

[3] C. M. Wang, X. Li, Z. Wang, W. Xu, J. Liu, F. Gao, L. Kovarik, J. G. Zhang, J. Howe, D. J. Burton, Z. Liu, X. Xiao, S. Thevuthasan, D. R. Baer, *Nano Lett.* **2012**, *12*, 1624.

[4] W. Zong, N. Chui, Z. Tian, Y. Li, C. Yang, D. Rao, W. Wang, J. Huang, J. Wang, F. Lai, T. Liu, *Adv. Sci.* **2021**, *8*, 2004142.

[5] K. Yan, Z. Lu, H. W. Lee, F. Xiong, P. C. Hsu, Y. Li, J. Zhao, S. Chu, Y. Cui, *Nat. Energy* **2016**, 1, 1-8.

[6] S. Liu, A. Wang, Q. Li, J. Wu, K. Chiou, J. Huang, J. Luo, *Joule* **2018**, 2, 184-193.

[7] W. Ye, F. Pei, X. Lan, Y. Cheng, X. Fang, Q. Zhang, N. Zheng, D. L. Peng, M. S. Wang, *Adv. Energy Mater.* **2020**, 10, 1902956.

[8] T. T. Zuo, Y. X. Yin, S. H. Wang, P. F. Wang, X. Yang, J. Liu, C. P. Yang, Y. G. Guo, *Nano Lett.* **2018**, 18, 297-301.

[9] H. Wang, Y. Li, Y. Li, Y. Liu, D. Lin, C. Zhu, G. Chen, A. Yang, K. Yan, H. Chen, Y. Zhu, J. Li, J. Xie, J. Xu, Z. Zhang, R. Vilá, A. Pei, K. Wang, Y. Cui, *Nano Lett.* **2019**, 19, 1326-1335.

[10] Z. Lu, S. Liu, C. Li, J. Huang, D. Wu, R. Fu, *Chem. Commun.* **2019**, 55, 6034-6037.

[11] Z. Wen, W. Fang, L. Chen, Z. Guo, N. Zhang, X. Liu, G. Chen, *Adv. Funct. Mater.* **2021**, 31, 2104930.

[12] T. Liu, J. Wang, Y. Xu, Y. Zhang, Y. Wang, *Nano-Micro Lett.* **2021**, 13, 1-13.

[13]G. Zheng, S. W. Lee, Z. Liang, H.-W. Lee, K. Yan, H. Yao, H. Wang, W. Li, S. Chu, Y. Cui, *Nat. Nanotechnol.* **2014**, 9, 618-623.