

## Supporting Information

# A 3D mixed ion/electron conducting scaffold by in-situ conversion for long-life lithium metal anodes

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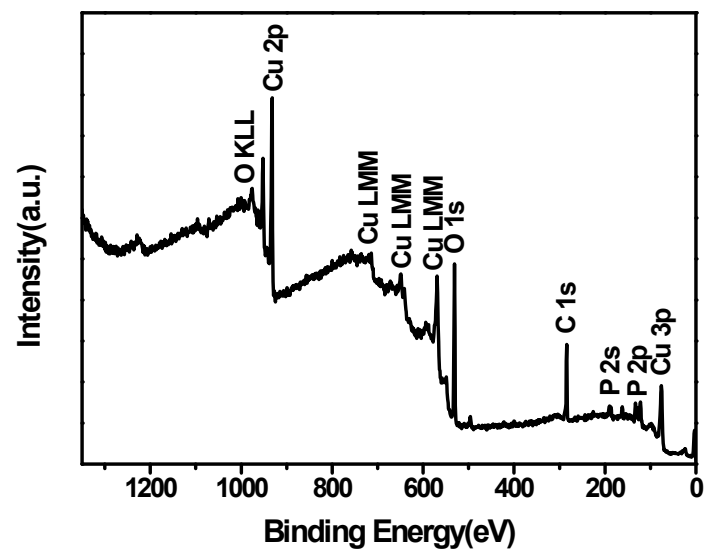
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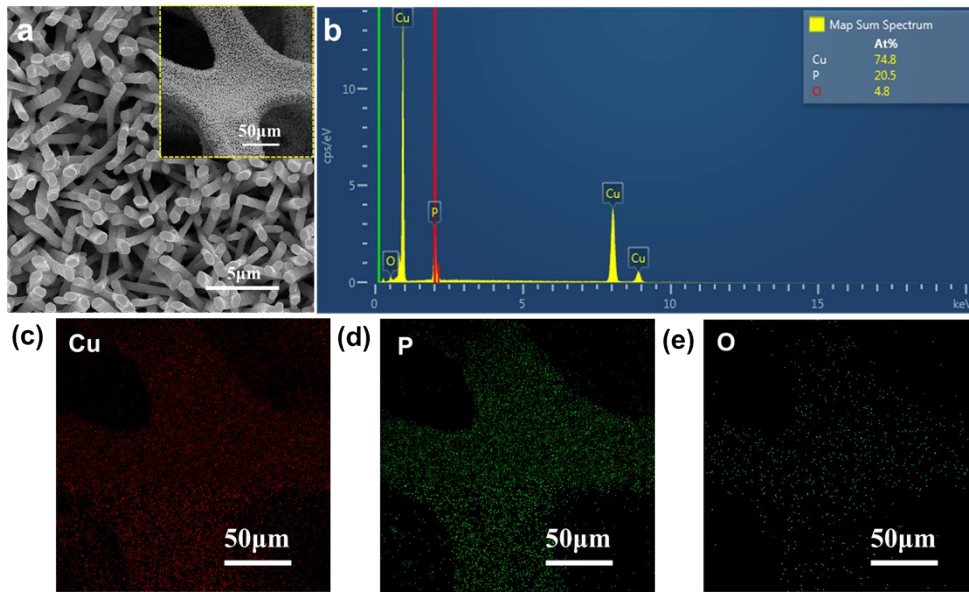
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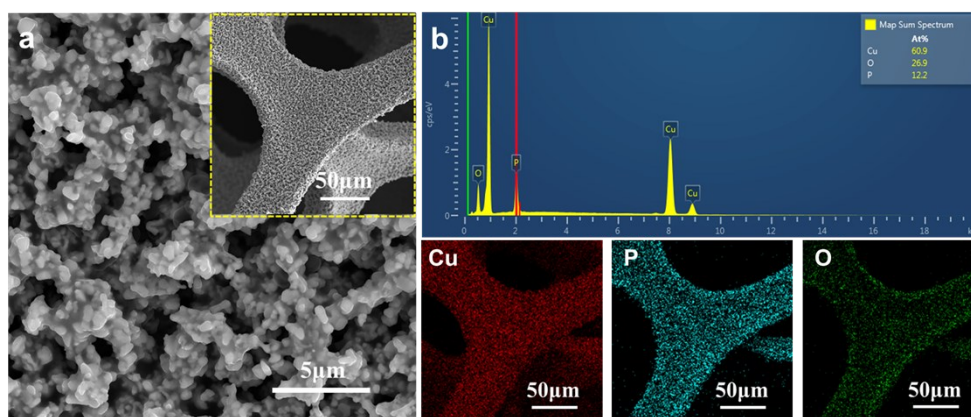
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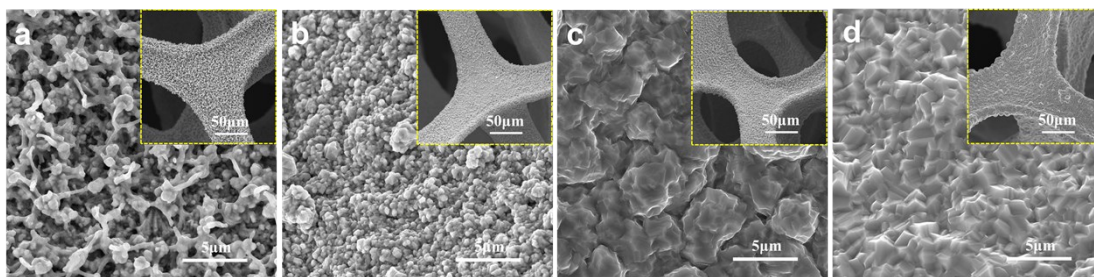
**Figure S1.** XPS full spectrum of as-synthesized Cu<sub>3</sub>P NA@CF.



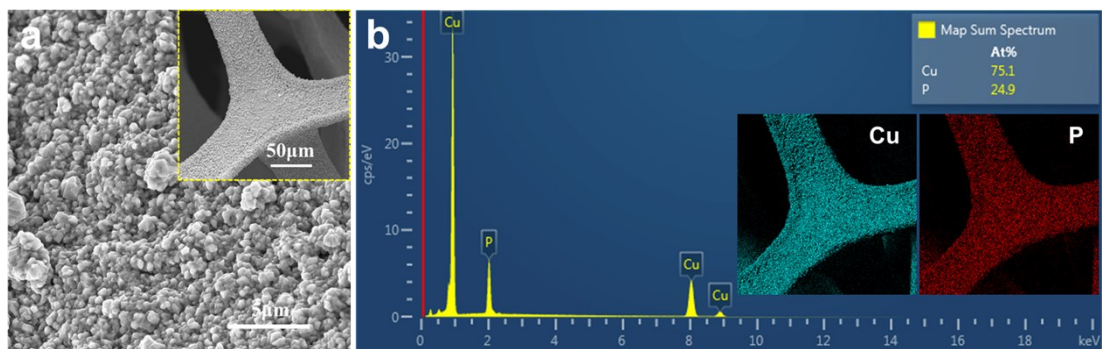
**Figure S2.** (a) SEM images of the  $\text{Cu}_3\text{P NA@CF}$  under the N/C of 1:1 at  $100^\circ\text{C}$ . (b) EDX spectrograms of  $\text{Cu}_3\text{P NA@CF}$  and corresponding elemental mapping images of Cu (c), P (d) and O (e).



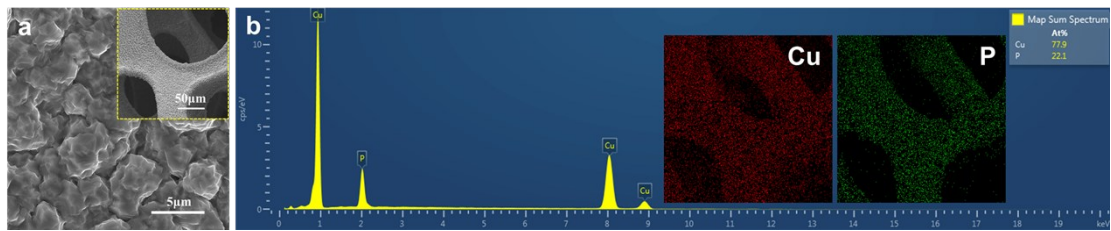
**Figure S3.** (a) SEM images of the  $\text{Cu}_3\text{P NA@CF}$  under the N/C of 1:2 at  $200^\circ\text{C}$ . (b) EDX spectrograms of  $\text{Cu}_3\text{P NA@CF}$  and corresponding elemental mapping images of Cu, P and O.



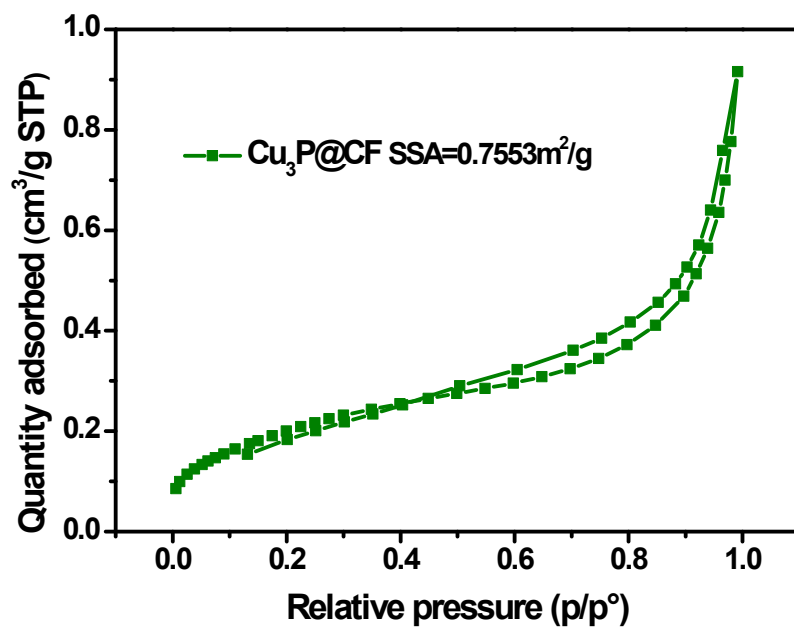
**Figure S4.** SEM image of the Cu<sub>3</sub>P NA@CF with different temperature of phosphating under the N/C of 3:1: (a) 220 °C; (b) 240 °C; (c) 260 °C; (d) 280 °C.



**Figure S5.** (a) SEM images of the Cu<sub>3</sub>P NA@CF under the N/C of 3:1 at 240°C. (b) EDX spectrograms of Cu<sub>3</sub>P NA@CF and corresponding elemental mapping images of Cu and P.



**Figure S6.** (a) SEM images of the Cu<sub>3</sub>P NA@CF under the N/C of 3:1 at 260°C. (b) EDX spectrograms of Cu<sub>3</sub>P NA@CF and corresponding elemental mapping images of Cu and P.



**Figure S7.** N<sub>2</sub> adsorption–desorption isotherm curve of Cu<sub>3</sub>P NA@CF under the N/C of 3:1 at 260°C.



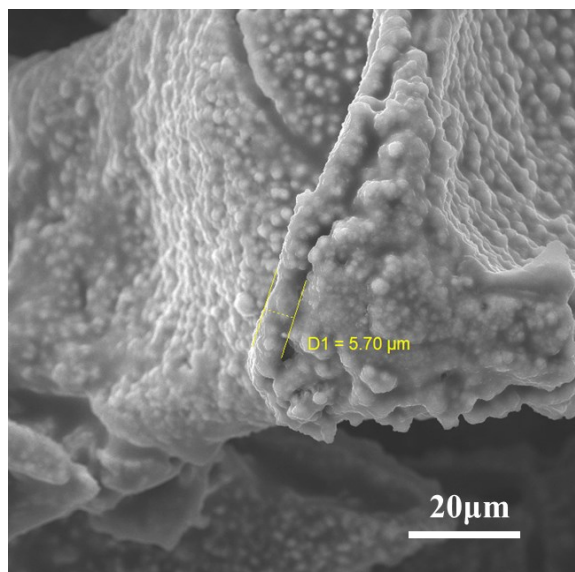
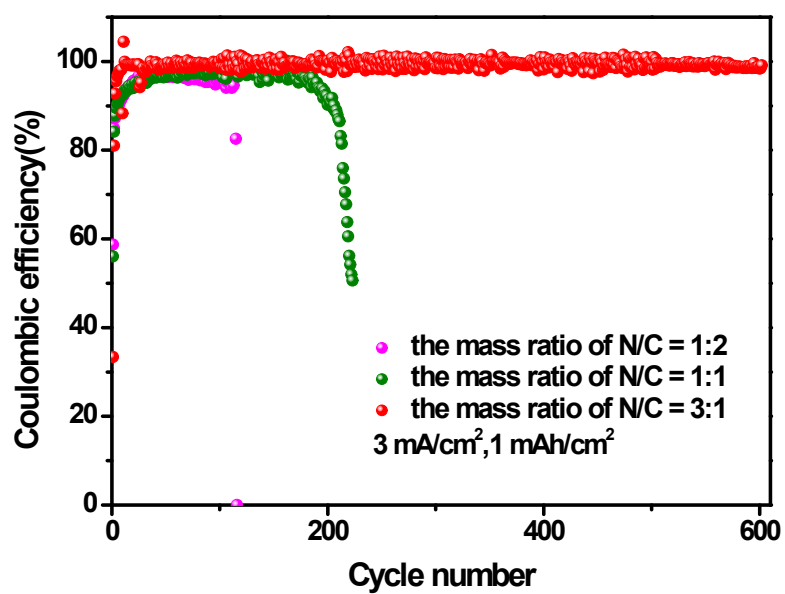
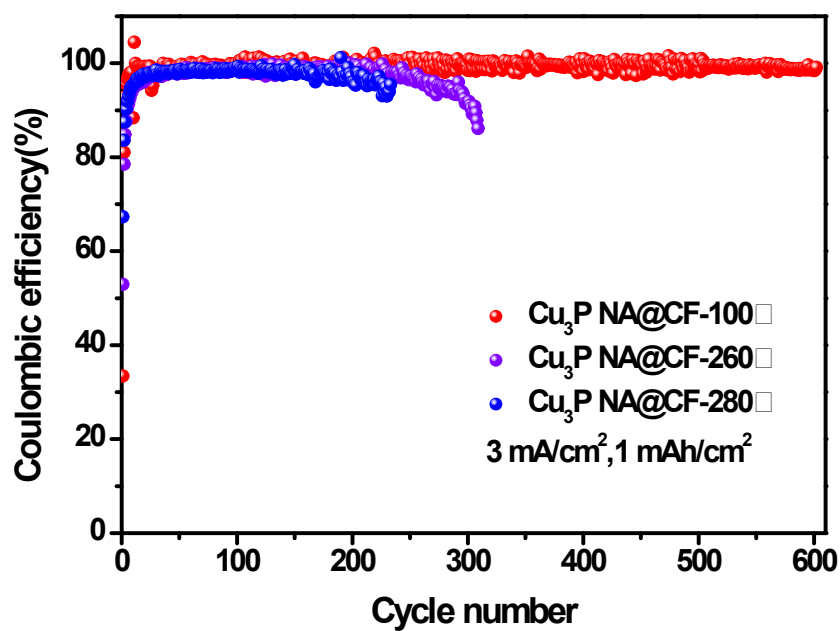


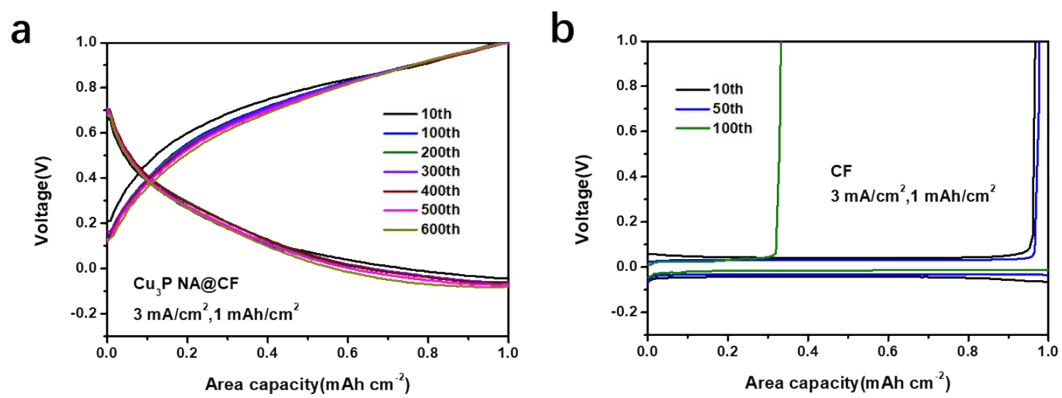
Figure S8. The thickness of Cu<sub>3</sub>P coating layer on Cu foam.



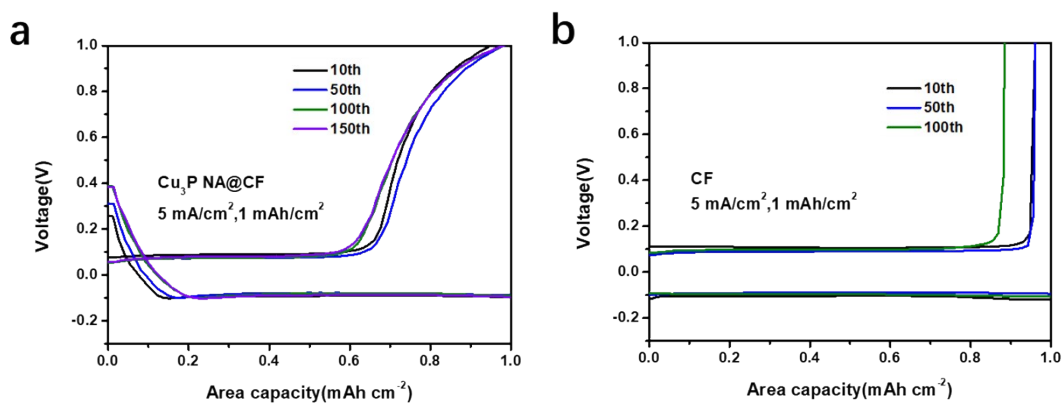
**Figure S9.** The Coulombic efficiency of  $\text{Cu}_3\text{P NA@CF}$  under the N/C of 1:2, 1:1 and 3:1 at  $3 \text{ mA cm}^{-2}$  for  $1 \text{ mAh cm}^{-2}$ .



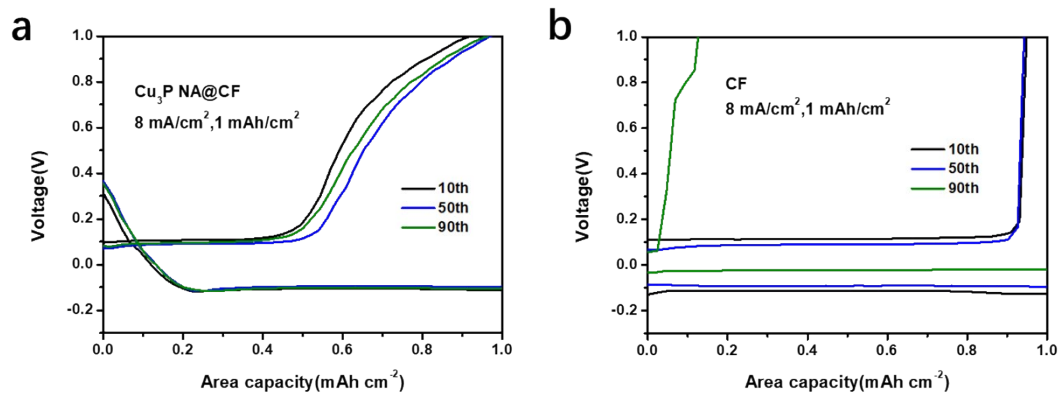
**Figure S10.** The Coulombic efficiency of the  $\text{Cu}_3\text{P NA@CF}$  with different temperature of phosphating under the N/C of 3:1 at  $3 \text{ mA cm}^{-2}$  for  $1 \text{ mAh cm}^{-2}$ .



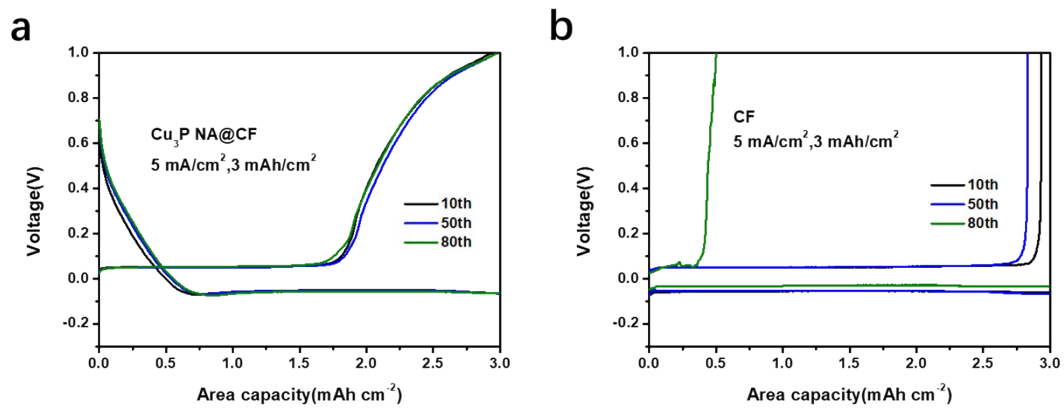
**Figure S11.** Voltage-capacity profiles for (a) PNF and (b) NF with a current density of 3 mA cm<sup>-2</sup> and a total capacity of 1 mAh cm<sup>-2</sup>.



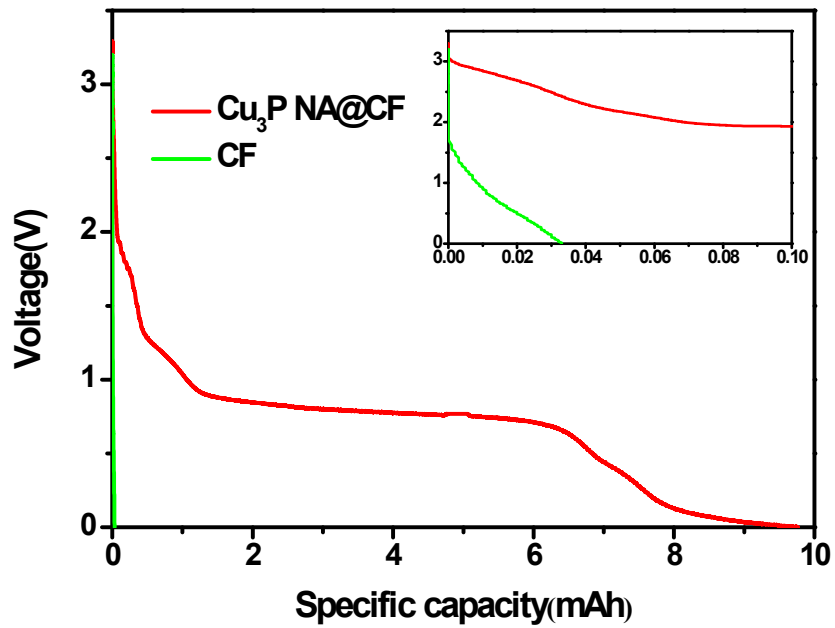
**Figure S12.** Voltage-capacity profiles for (a) PNF and (b) NF with a current density of 5 mA cm<sup>-2</sup> and a total capacity of 1 mAh cm<sup>-2</sup>.



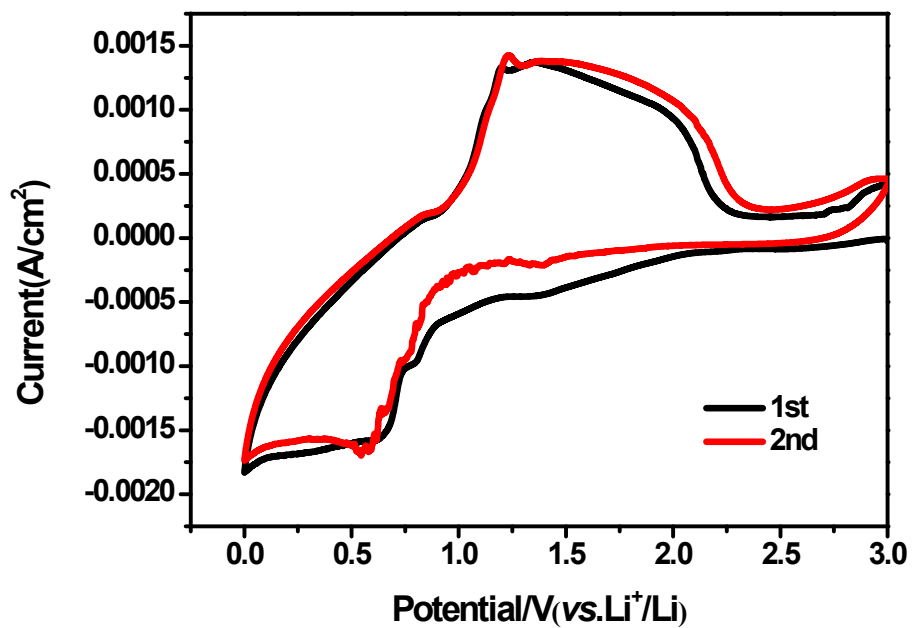
**Figure S13.** Voltage-capacity profiles for (a) PNF and (b) NF with a current density of  $8 \text{ mA cm}^{-2}$  and a total capacity of  $1 \text{ mAh cm}^{-2}$ .



**Figure S14.** Voltage-capacity profiles for (a) PNF and (b) NF with a current density of  $5 \text{ mA cm}^{-2}$  and a total capacity of  $3 \text{ mAh cm}^{-2}$ .

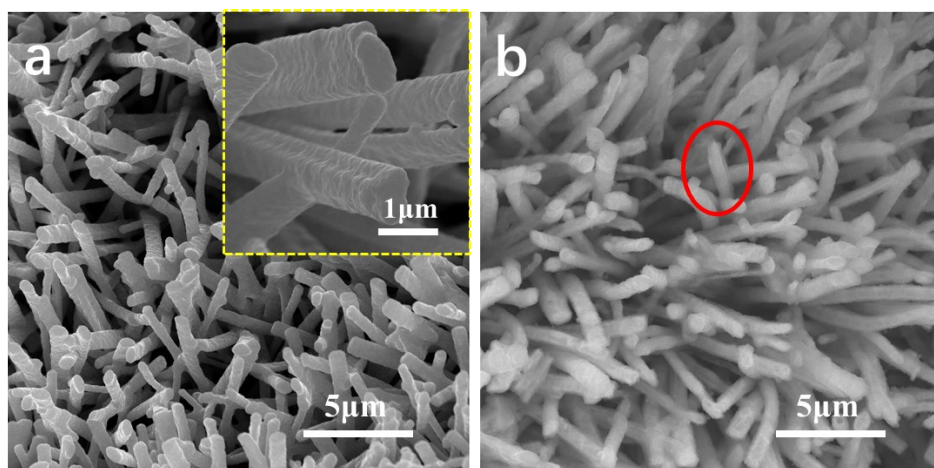


**Figure S15.** The voltage–capacity curves of  $\text{Cu}_3\text{P NA@CF}$  in the first Li deposition.

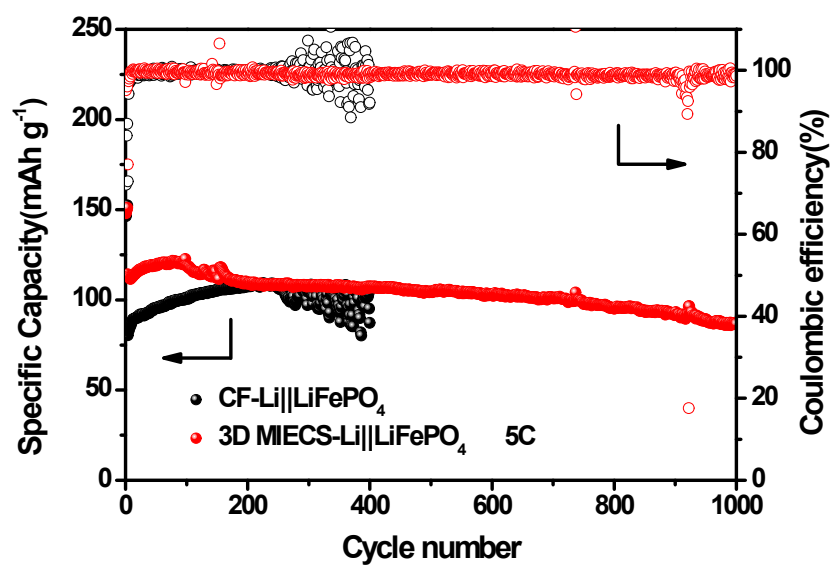


**Figure S16.** CV curves of the lithiation and delithiation of Cu<sub>3</sub>P NA@CF at a sweep speed of 0.1 mV s<sup>-1</sup> from 0.01 to 3.0 V (vs. Li<sup>+</sup>/Li).

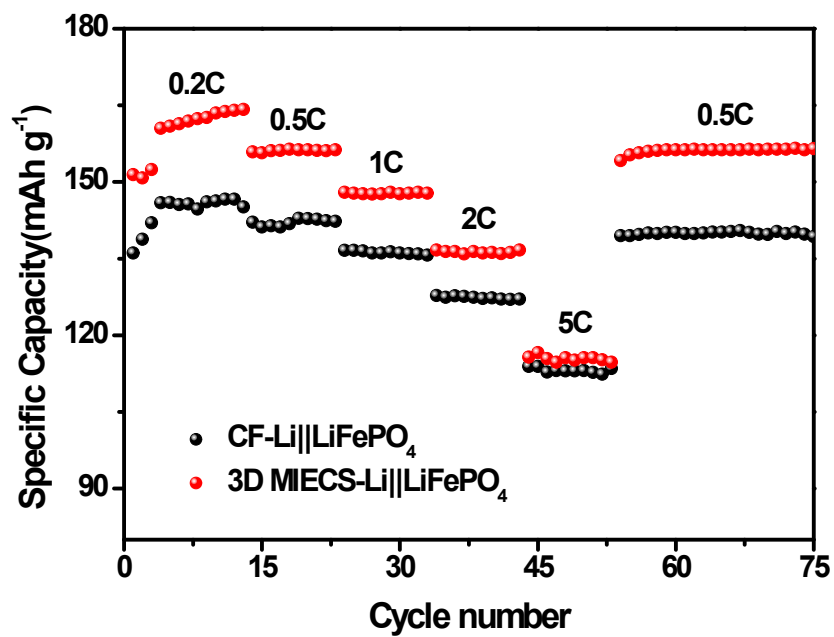




**Figure S17.** Magnification SEM images of the pristine and 200th stripping on Cu<sub>3</sub>P NA@CF at 3 mA cm<sup>-2</sup> with a total capacity of 1 mAh cm<sup>-2</sup>.



**Figure S18.** The cycling performance of 3D MIECS-Li||LiFePO<sub>4</sub> and CF-Li||LiFePO<sub>4</sub> cell at 5 C.



**Figure S19.** Rate performance between 3D MIECS-Li||LiFePO<sub>4</sub> and CF-Li||LiFePO<sub>4</sub> cell

## Li metal-based anodes reported recently

Materials	Current density&Capacity	Cycle number	CE (%)	references
Unique 3D nanoporous/macroporous structure Cu current collector	1 mA cm <sup>-2</sup> , 1 mAh cm <sup>-2</sup>	200	98	[1]
nitrogen-doped-carbon/ZnO modified Cu foam	3 mA cm <sup>-2</sup> , 1 mAh cm <sup>-2</sup>	400	97.6	[2]
Cu <sub>2</sub> S nanowires inside the Cu framework	3 mA cm <sup>-2</sup> , 1 mAh cm <sup>-2</sup>	100	92	[3]
Lithiophobic-lithiophilic composite architecture	1.5 mA cm <sup>-2</sup> , 1 mAh cm <sup>-2</sup>	200	98	[4]
	5 mA cm <sup>-2</sup> , 3 mAh cm <sup>-2</sup>	50	96	
3D porous Cu current collector	0.5 mA cm <sup>-2</sup> , 1 mAh cm <sup>-2</sup>	70	97	[5]
A self-supported, three-dimensional porous copper film	1 mA cm <sup>-2</sup> , 1 mAh cm <sup>-2</sup>	97	120	[6]
Hierarchically Bicontinuous Porous Copper as Advanced 3D Skeleton	3 mA cm <sup>-2</sup> , 1 mAh cm <sup>-2</sup>	94	100	[7]
	3 mA cm <sup>-2</sup> , 1 mAh cm <sup>-2</sup>	600	99.1	
A 3D mixed ion/electron conducting scaffold by in-situ conversion	5 mA cm <sup>-2</sup> , 1 mAh cm <sup>-2</sup>	170	98.2	this work
	5 mA cm <sup>-2</sup> , 3 mAh cm <sup>-2</sup>	80	99.35	

## References

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