## **Supporting Information**

## Stable Li metal anode in a lithiophilic shuttle

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Figure S1. (a) XRD patterns and (b) XPS spectra of CF@Cu and CF@L-Cu.



Figure S2. (a) XRD patterns, (b) Raman spectra and (c) SEM images of CF@CuO and CF@L-CuO.



Figure S3. N2 adsorption isotherm of CF@CuO and CF@L-CuO from BET measurements.



Figure S4. Voltage profiles of Li plating on CF, CF@CuO and CF@L-CuO.



Figure S5. XRD pattern of the lithiated CF@L-CuO.



Figure S6. Cu 2p and O 1s XPS spectra of CF@L-CuO before and after lithiation process.

![](_page_7_Picture_0.jpeg)

Figure S7. Digital photos of CF, CF@Cu, CF@CuO and CF@L-CuO deposited on molten Li.

![](_page_8_Figure_0.jpeg)

**Figure S8.** Discharge/charge curves of Li plating/stripping of Li metal half cells using CF, CF@CuO or CF@L-CuO as working electrodes, under (a) 0.5 mA cm<sup>-2</sup> – 1 mAh cm<sup>-2</sup>, (b) 1 mA cm<sup>-2</sup> – 2 mAh cm<sup>-2</sup> and (c) 3 mA cm<sup>-2</sup> – 1.5 mAh cm<sup>-2</sup>.

![](_page_9_Figure_0.jpeg)

Figure S9. Nyquist plots from EIS data of CF, CF@CuO and CF@L-CuO at different cycling states. The cycling was carried out under 0.5 mA cm<sup>-2</sup> - 1 mAh cm<sup>-2</sup>.

![](_page_9_Figure_2.jpeg)

Figure S10. Voltage profiles of Li/CF||Li/CF, Li/CF@CuO||Li/CF@CuO and Li/CF@L-CuO||Li/CF@L-CuO symmetrical cells cycling at 0.5 mA cm<sup>-2</sup> for a fixed capacity of 1 mAh cm<sup>-2</sup>.

![](_page_10_Figure_0.jpeg)

**Figure S11.** SEM images of CF, CF@CuO and CF@L-CuO disassembled from the half cells at different cycling states. The cycling was carried out under 0.5 mA cm<sup>-2</sup> - 1 mAh cm<sup>-2</sup>.

![](_page_11_Figure_0.jpeg)

Figure S12. Charge/discharge curves of Li metal full cells using Li, Li/CF@CuO or Li/CF@L-CuO anodes and NCA cathodes (~ 5 mAh cm<sup>-2</sup>), at charge/discharge rates of 0.1C/0.1C (0.5 mA cm<sup>-2</sup>/0.5 mA cm<sup>-2</sup>).

![](_page_12_Figure_0.jpeg)

Figure S13. Charge/discharge curves of Li metal full cells using Li, Li/CF@CuO or Li/CF@L-CuO anodes and NCA cathodes (~ 5 mAh cm<sup>-2</sup>), at charge/discharge rates of (a) 0.2C/0.2C (1 mA cm<sup>-2</sup>/1 mA cm<sup>-2</sup>), (b) 0.4C/0.4C (2 mA cm<sup>-2</sup>/2 mA cm<sup>-2</sup>) and (c) 0.6C/0.6C (3 mA cm<sup>-2</sup>/3 mA cm<sup>-2</sup>).

![](_page_13_Figure_0.jpeg)

**Figure S14.** Cycling performances of Li metal full cells using NCA cathodes (~ 5 mAh cm<sup>-2</sup>) with an N/P ratio of 2, in (a) carbonate electrolyte and (b) LHCE. The cycling test was carried out at charge/discharge rates of 0.2C/0.2C (1 mA cm<sup>-2</sup>/1 mA cm<sup>-2</sup>).