## Supplementary Information

## Graphene Anchored on Cu Foam as Lithiophilic 3D Current Collectors for Stable and Dendrite-free Lithium Metal Anode

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Fig. S1. N<sub>2</sub> sorption isotherms of Cu foam and GN@Cu foam.



Fig. S2. Raman spectra of GN@Cu foam before and after 10 cycles.



Fig. S3. EDS mapping of GN@Cu foam: b) Copper and c) carbon distribution in the selected area



Fig. S4. a-c) Voltage profiles of Li plating/stripping on Cu foam and GN@Cu foam electrodes in the first cycle at 0.5 mA cm<sup>-2</sup>, 1 mA cm<sup>-2</sup> and 5 mA cm<sup>-2</sup>, respectively. d-f) Cycling performance comparison of Cu foam and GN@Cu foam electrodes in half cells at different current densities.



Fig. S5. a) Cycling performance comparison of Li plating/stripping at 4 mA cm<sup>-2</sup> for 1 mAh cm<sup>-2</sup> on Li foil and GN@Cu foam Li electrodes in symmetric cells. b) Detailed voltage profiles of Li foil and GN@Cu foam Li electrodes in different cycles.



Fig. S6. Sectional SEM image of GN@Cu foam, showing the thickness of GN@Cu foam is 270  $\mu m.$ 



Fig. S7. Voltage profiles of Li plating/stripping on Cu foam and GN@Cu foam electrodes in the 100th cycle at 2 mA cm<sup>-2</sup>.



Fig. S8. a) Voltage profiles of Li plating/stripping on Cu foam and GN@Cu foam electrodes in the first cycle at 1 mA cm<sup>-2</sup> for 5 mAh cm<sup>-2</sup> Li. b) Cycling performance comparison of Cu foam and GN@Cu foam electrodes in half cells at 1 mA cm<sup>-2</sup>.



Fig. S9. Cycling performance of Li plating/stripping at 0.5 mA cm<sup>-2</sup> for 1 mAh cm<sup>-2</sup> on Cu foil Li electrodes in symmetric cells.



Fig. S10. Voltage profiles of Li plating/stripping at 10 mA cm<sup>-2</sup> for 10 mAh cm<sup>-2</sup> on GN@Cu foam Li electrodes in symmetric cells.



Fig. S11. a) Charge/discharge curves of the Cu foil Li/LFP and GN@Cu foam Li/LFP full cells at 0.2 C. b) Cycling performance of Cu foil Li /LFP and GN@Cu foam Li/LFP full cells at 0.2 C.

To study the superiority of lithiophilic host, cycling performance in carbonate electrolyte (1 M LiPF<sub>6</sub> in EC/DEC, 1:1 by volume ratio) is shown in Fig. S12. It can be seen that GN@Cu foam exhibits lower nucleation overpotential and better cycling stability compared to Cu foam, confirming the lithiophilic property of GN@Cu foam. It is worth mentioning that the CE of these materials in carbonate electrolyte is lower than that in ether electrolyte, which indicates that ether electrolyte and LiNO<sub>3</sub> additive are favorable for Li plating/stripping.



Fig. S12. a) Voltage profiles of Li plating/stripping on Cu foam and GN@Cu foam electrodes in the first cycle at 0.5 mA cm<sup>-2</sup> in carbonate electrolyte. b) Cycling performance comparison of Cu foam and GN@Cu foam electrodes in half cells at 0.5 mA cm<sup>-2</sup>.