Supporting Information

Substrate-Influenced Three-Dimensional Unoriented Dispersion

Pathway for Dendrite-Free Lithium Metal Anode

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Supplementary figures and tables



Figure S1. A schematic of the procedures to synthesis of MnO₂-Cu.



Figure S2. Digital pictures of (a) scale-up MnO₂-Cu; (b) MnO₂-Cu after friction for 1 min; (c) MnO₂-Cu after friction for 20 min.



Figure S3. (a,d) Cross-section and Top-view images of MnO₂-Cu prepared with original concentration of reagents and a reaction time of 12 h. (b,e) MnO₂-Cu prepared with doubled concentration of reagents. (c,f) MnO₂-Cu prepared with an increased reaction time of 24 h.

Unlike the process of doctor-blade casting, the thickness of MnO₂ layer can be hardly changed by a method of making the MnO₂ nanosheets in-situ grow onto the Cu foil and then removing the extra MnO₂ loosely attached with the Cu by ultrasonication. Neither changing the concentration of reagents nor adjusting the reaction time can change the thickness of MnO₂ layer. The morphology of MnO₂ nanosheets can be changed under these different conditions (Figure S3e and S3f), but they cannot provide regular pathways as Figure S3d.



Figure S4. (a) N_2 adsorption-desorption isotherms and (b) corresponding pore size distributions of MnO_2 stretched away from Cu foil.

The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method based on a multipoint analysis, and the pore size distribution was determined using Density-functional-theory (DFT) method. The specific surface area is $38.8 \text{ m}^2 \text{ g}^{-1}$.



Figure S5. X-ray diffraction pattern of MnO₂ stretched from Cu foil.



Figure S6. (a) AFM image of bare copper foil. (b) AFM image of MnO₂-Cu. (c) A photography

picture and (b) top-view SEM image of surface.

Materials	$c_0 (mg L^{-1})$	$c_e (mg L^{-1})$	$\Delta c (mg L^{-1})$	Q (mg g ⁻¹)
Glass bottle	84.892	82.501	2.391	-
Cu	84.892	82.555	2.337	0
δ-MnO ₂	84.892	74.821	10.071	38.4

Table S1. Li⁺ adsorption properties of Cu and MnO₂.

In the Li⁺ adsorption properties test, adsorption process was conducted in 200 mL glass bottles containing 100 mL 0.5 mg mL-1 LiCl aqueous solution. Due to the slight adsorption capacity of glass, the results should eliminate the influence of glass. The Adsorption property values will be calculated from the change of solution concentration using the following equation:

$$Q = \frac{(c_e - c_{e,bottle})V}{m}$$

Equation 1



Figure S7. (a) The voltage profiles of tested batteries that were first cycled at 0-1 V (vs. Li+/Li) at 50 μ A for five cycles for the contamination removal and interface stabilization. (b) CV profiles of a half cell using MnO₂-Cu as working electrode.

The CV test was performed at a scan rate of 0.2 mV s^{-1} , and with a cut-off voltage of $-0.5 \sim 3$ V, which totally covers the oxidation-reduction potential of anode. The CV result could prove that the MnO₂ thin layer would not act as an active anode material.



Figure S8. (a, b) AFM images of initial Cu foil and Cu after deposited 1 mAh of Li. (c)

Surface roughness of bare Cu and MnO₂-Cu before and after different Li deposition.



Figure S9. SEM images of Li plated on MnO_2 -Cu at a current density of (a, b) 0.5 mA cm⁻² and (c, d) 3 mA cm⁻².



Figure S10. SEM image of Li deposited on (a) bare Cu foil and (b) MnO₂-Cu in carbonatebased electrolyte.

The specific composition of the electrolyte is 1 M LiPF₆ dissolved in a mixed solvent of EC, DEC and EMC (1:1:1, v/v).



Figure S11. SEM image of MnO₂-Cu after 100th stripping.



Figure S12. XPS spectra of Li metal anode on the 3D Cu foil after 10 cycles. (a) Survey, (b) C 1s, (c) F 1s and (d) Li 1s spectra of the SEI layer covered on Li anode.



Figure S13. Voltage hysteresis of Li plating/stripping at (a) 0.5 mA cm^{-2} and (b) 3 mA cm^{-2} on MnO₂-Cu or bare Cu foil.



Figure S14. Voltage profiles of plating/stripping process with (a, b) 0.5 mA cm^{-2} and (c, d) 3 mA cm⁻² for 1 mAh cm⁻² of Li on MnO₂-Cu and bare Cu foil.



Figure S15. The equivalent circuit for Nyquist plots in Figure 6b.

Table S2. Electrochemical impedance fitted parameters for Figure 6 with an equivalent circuitmodel in Figure S15.

	Bare Cu			MnO ₂ -Cu		
	R _b	R _{SEI}	R _{ct}	R _b	R _{SEI}	R _{ct}
Before cycle	3.31	-	60.15	2.18	-	30.56
After 50th cycle	26.61	15.59	33.38	2.40	20.62	4.53



Figure S16. Coulombic efficiency of cells using bare Cu and MnO₂-Cu at (a, d) 0.5 mA cm^{-2} , (b, e) 1.0 mA cm⁻² and (c, f) 3.0 mA cm⁻² for a total of 3.0 and 5.0 mAh cm⁻² of Li.



Figure S17. Voltage profiles of symmetric cell using bare Cu and MnO_2 -Cu at a current density of 1 mA cm⁻² and 3 mA cm⁻² for Li capacity loading of (a, b) 1 mAh cm⁻² and (c, d) 3 mAh cm⁻²



Figure S18. (a) Cycling performance and (b) rate capability of the LiFePO₄/Li cells with bare Cu foil and MnO₂-Cu.