

## **Uniform Li Deposition Regulated via Three-Dimensional Polyvinyl Alcohol Nanofiber Network for Effective Li Metal Anodes**

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### **Experimental**

#### **Method**

10 wt% PVA (M<sub>w</sub>=89000~98000, 99% degree of hydrolysis, Aldrich) solution was prepared by dissolving of 1.0 g PVA into 9 mL H<sub>2</sub>O at 95 °C with vigorous stirring overnight. Afterwards, the solution was transferred to an injector (5 mL) with a single-nozzle ( $\phi=0.41$  mm) for electrospinning. The applied voltage on the needle, the solution flow rate, and the distance between the needle tip and the copper collector were 12 kV, 0.6 mL h<sup>-1</sup>, and 15 cm, respectively. After 5 h of electrospinning, the obtained material was transfer to a vacuum at 80 °C for 12 h to remove the residual water, and then the preparation of PVA nanofiber modified Cu collector was achieved, denoted by PVA-Cu.

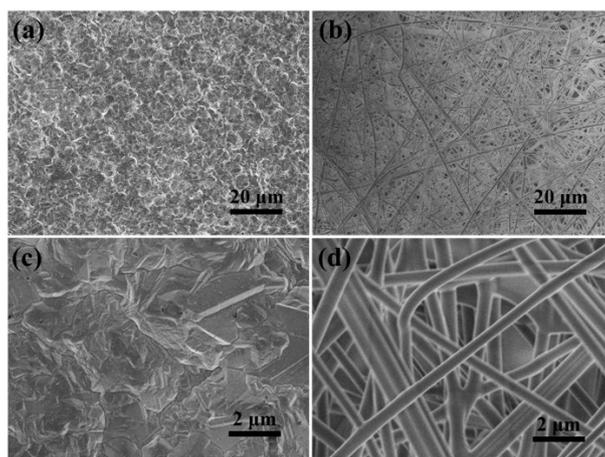
## **Material characterization**

The morphology and microstructure were investigated by field-emission scanning electron microscope (FE-SEM, Hitachi SU8010). Note that all the batteries after cycled were disassembled and rinsed with anhydrous dimethyl carbonate (DMC) to remove remnant lithium salts and electrolyte in glovebox before to observe the morphology. The FT-IR testing of the as-prepared material was performed by Perkin Elmer spectrometer. Raman measure was manipulated under the Renishaw RM1000 micro spectroscopic system. The X-ray diffraction (XRD) technique was carried out on the Bruker D8 Advance (Germany) using Cu K $\alpha$  radiation ( $\lambda=1.54178 \text{ \AA}$ ) between  $10^\circ$  and  $80^\circ$  ( $2\theta$ ).

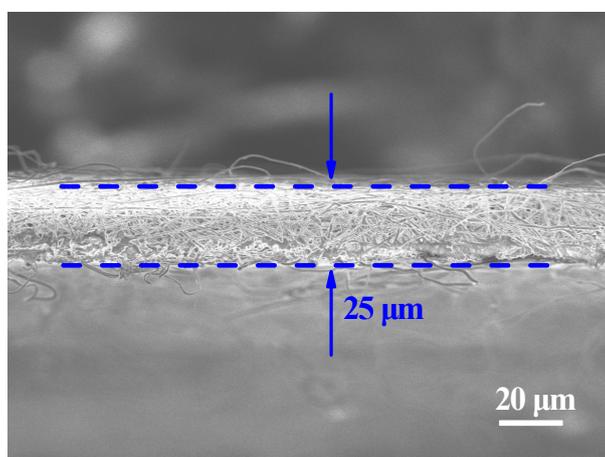
## **Electrochemical measurements**

2032-type coin cells were employed in Ar-filled glovebox to test the electrochemical property of the as-prepared materials. The electrolyte was 1 M lithium bis(trifluoromethane) sulfonamide (LiTFSI, Aldrich) in a mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 in volume ratio) with 3 wt% LiNO<sub>3</sub> as an additive, and the separator was porous polypropylene based membrane (Celgard) with a thickness of 25  $\mu\text{m}$ . Galvanostatic tests were monitored using a LAND CT2001A battery-testing system, metallic copper foil ( $\Phi 12 \text{ mm}$ ) and PVA-Cu were used as the working electrode, and Li metal anode ( $\Phi 15 \text{ mm}$ ) as the counter electrode. For Coulombic efficiency (CE) testing, a constant deposition capacity of Li (1 or 3 mAh cm<sup>-2</sup>) with various current densities (1, 3, or 5 mA cm<sup>-2</sup>) was plated onto the Cu or PVA-Cu electrode and then stripped away up to 1 V. For the symmetric tests, the

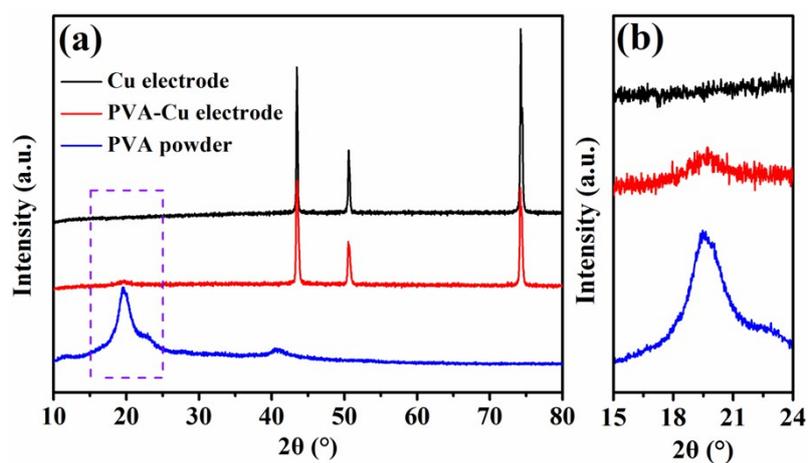
PVA nanofiber film was peeled off from Cu collector and implanted onto the surface of Li anode, and then the symmetric test of PVA-Li was performed at a current density of  $5 \text{ mA cm}^{-2}$  with a fixed deposition capacity (1 or  $2 \text{ mAh cm}^{-2}$ ).



**Fig. S1.** SEM images of (a, c) bare Cu and (b, d) PVA-Cu electrodes before cycling at different magnification.



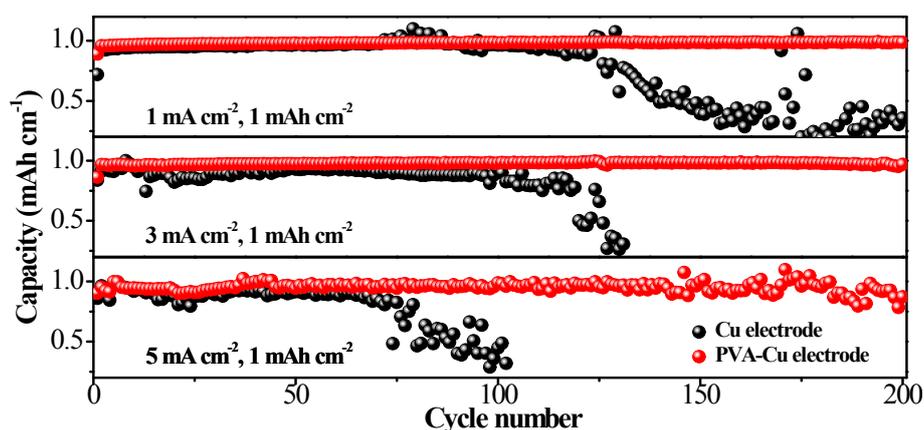
**Fig. S2.** Cross-sectional SEM image of the PVA film.



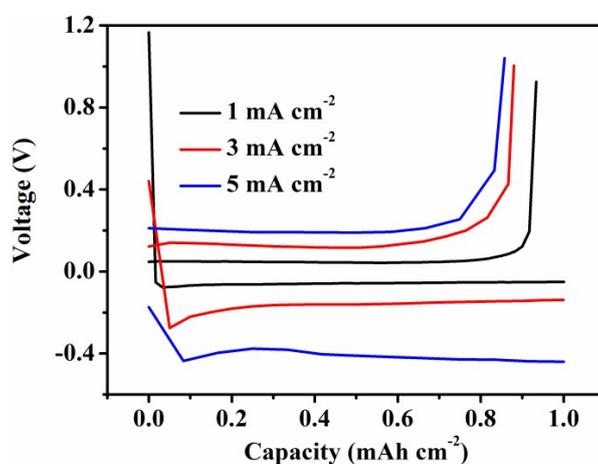
**Fig. S3.** (a) XRD diffraction pattern of bare Cu electrode, PVA-Cu electrode, and PVA powder, (b) the enlarged image for the circled region in (a).

**Table S1** Cyclic stability and CE comparisons of the PVA-Cu electrode with previously reported works on Li metal anode.

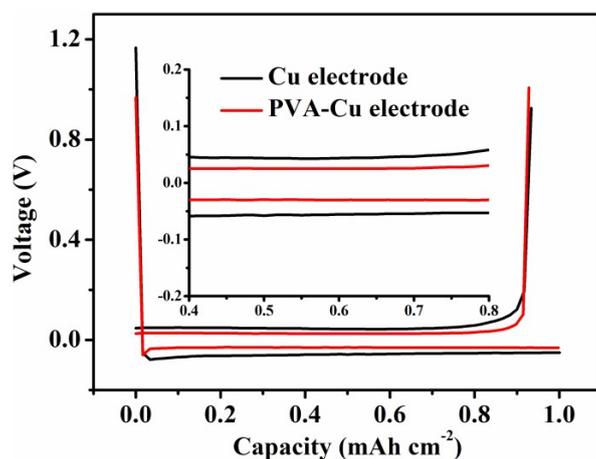
Current density (mA cm <sup>-2</sup> )	Deposition capacity (mAh cm <sup>-2</sup> )	Cycle number	CE (%)	References
0.5	1	100	93.8	Ref.33
1	1	>120	97.9	Ref.44
0.5	1	120	97.2	Ref.45
5	0.5	60	92.6	Ref.46
1	1	140	97	Ref.47



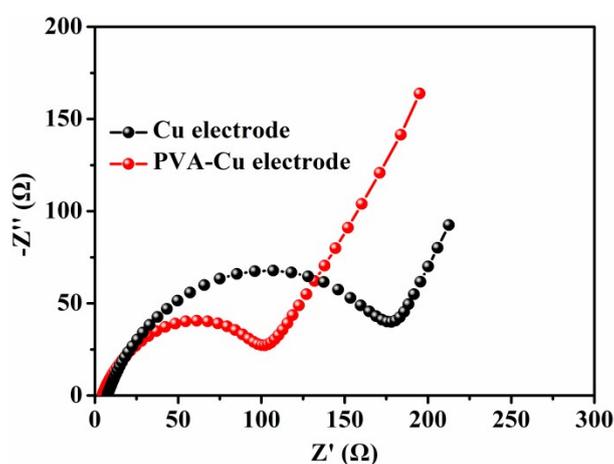
**Fig. S4.** Cycling performance of bare Cu and PVA-Cu electrodes at various current densities.



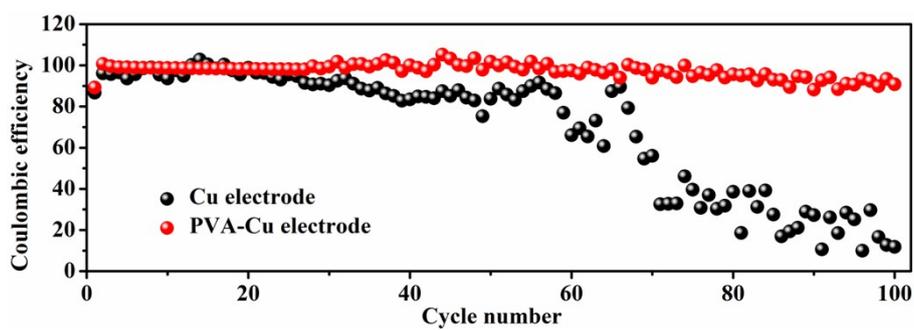
**Fig. S5.** Voltage profiles of the plating/stripping for bare Cu electrode at various current densities.



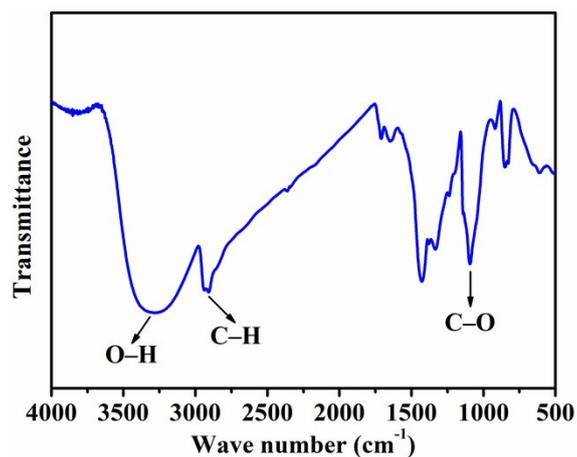
**Fig. S6.** Comparison of the initial voltage profiles of bare Cu and PVA-Cu electrodes with current density of  $1 \text{ mA cm}^{-2}$ , the inset presents enlarged profiles.



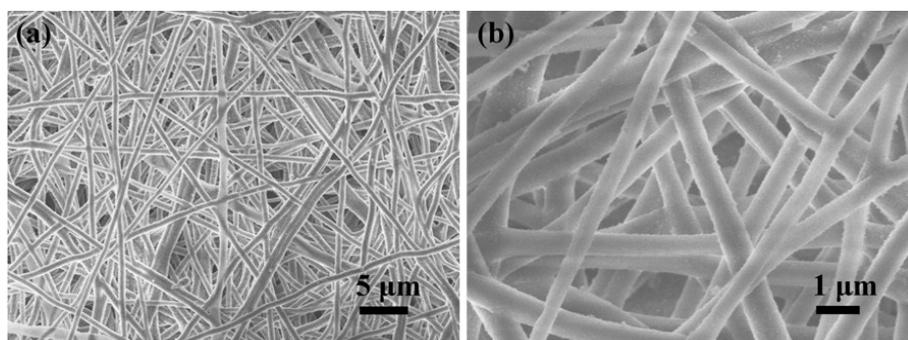
**Fig. S7.** EIS of bare Cu and PVA-Cu electrodes after 10 cycles.



**Fig. S8.** Comparison of CEs of Li deposition on Cu electrode with and without PVA coating at a current density of  $3 \text{ mA cm}^{-2}$  under deposition capacity of  $3 \text{ mAh cm}^{-2}$ .

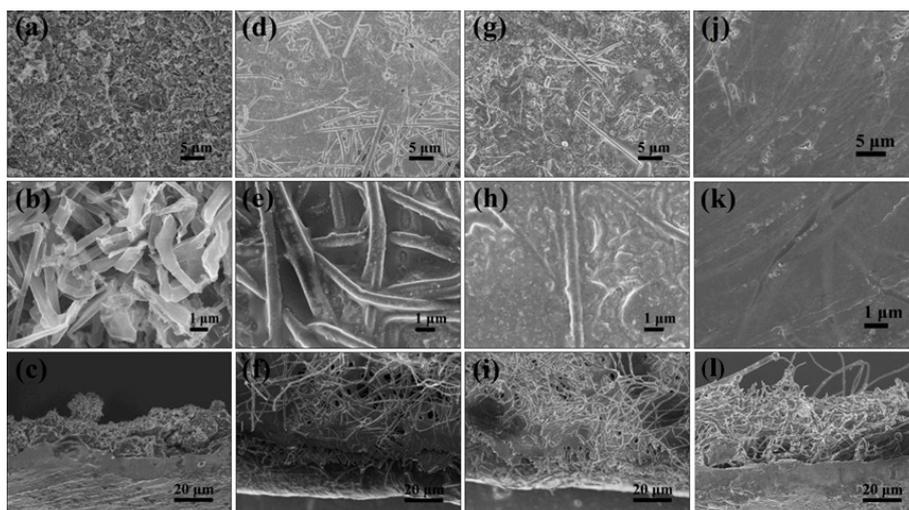


**Fig. S9.** FT-IR spectrum of PVA film after 200 cycles at a current density of 3 mA cm<sup>-2</sup>.

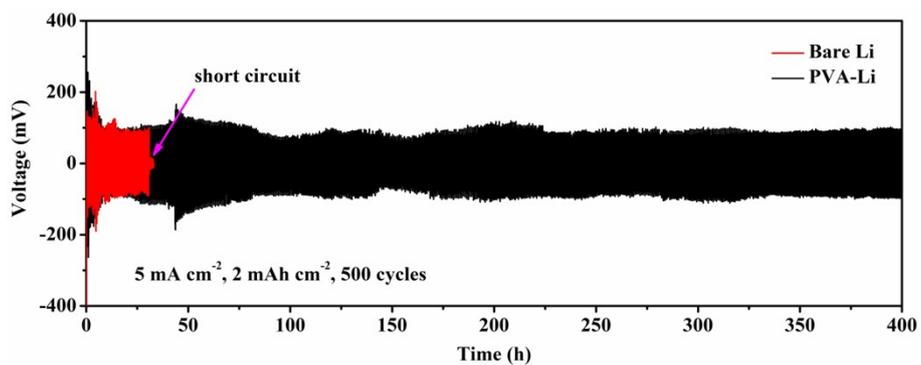


**Fig. S10.** SEM images of PVA film after 200 cycled at (a) low and (b) high magnifications.

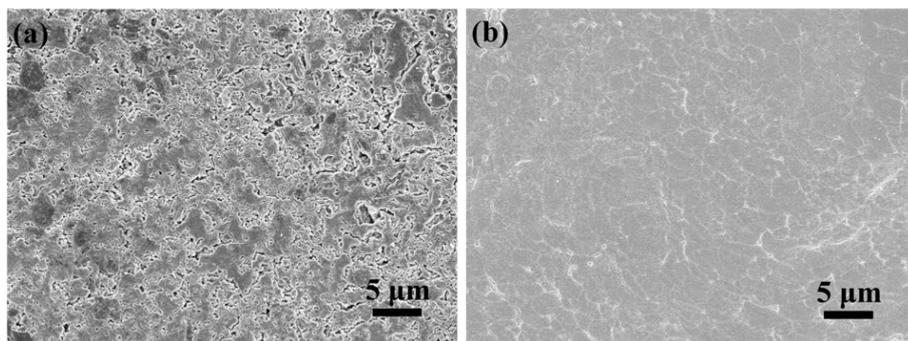
First of all, the cells after cycled were disassembled and rinsed with anhydrous DMC to remove remnant Li salts and electrolyte in glovebox. Then, the electrodes were immersed in water to react the deposited Li. After drying for 24 h, the variations of functional group and morphology of PVA film were detected by FT-IR and FE-SEM analysis.



**Fig. S11.** SEM images of Li deposit on Cu foil with or without PVA coating after 100 cycles at various current densities with a deposition capacity of  $1 \text{ mAh cm}^{-2}$ . (a, b) Top and (c) cross-section of bare Cu electrode after 100 cycles at a current density of  $1 \text{ mA cm}^{-2}$ ; (d, e) Top and (f) cross-section of PVA Cu electrode after 100 cycles at a current density of  $1 \text{ mA cm}^{-2}$ ; (g, h) Top and (i) cross-section of PVA Cu electrode after 100 cycles at a current density of  $3 \text{ mA cm}^{-2}$ ; (j, k) Top and (l) cross-section of PVA-Cu electrode after 100 cycles at a current density of  $5 \text{ mA cm}^{-2}$ .



**Fig. S12.** Cycling stability of symmetric cell using (a) bare Li and (b) PVA-Li anodes at a current density of  $5 \text{ mA cm}^{-2}$  with a deposition capacity of  $2 \text{ mAh cm}^{-2}$ .



**Fig. S13.** SEM images of symmetric cell using (a) bare Li and (b) PVA-Li electrodes after 100 cycles at low magnification.