Supporting Information

Ex-situ identification of Cu^+ long-range diffusion path of Cu-based anode for lithium ion battery

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Experimental Section

Synthesis of CuO microsheet array: Prior to the synthesis of CuO, high-purity copper substrates (99.99% purity) were carefully cleaned with absolute alcohol and deionized water, respectively, in an ultrasound bath to remove surface impurities. The growth solution was prepared by mixing 0.46g $(NH_4)_2S_2O_8$, 1.0g NaOH and 15.0 ml water. Then, Cu foils were immersed into the above mixed solution for 40h. Black CuO was grown on these Cu foils.

Electrochemical cell test: CuO grown on these Cu foils form the integrated anode materials, which were cut into discs and used directly as the working electrode without binders and conductivity agents. Lithium metal was used as the counter and reference electrode, Celgard 2400 was used as separator, the electrolyte is 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC/DMC/DEC, 1:1:1 vol%). The mass of active CuO materials was determined from the weight difference of these CuO films before and after the acid washing treatment. A galvanostatic cycling test of these assembled half-cells was conducted on a LAND CT2001A system in the voltage range of 0.01–3.0 V (vs. Li^+/Li). Cyclic

voltammogram (CV) tests were recorded on an electrochemical workstation (CHI, 660D) between 3.0 and 0.01 V at the scan rate of 0.1 mV s^{-1}.

Characterization: Surface morphology and chemical composition of the as-obtained CuO nanosheet films were examined using a field-emission scanning electron microscope (FESEM, Hitachi-S4800), a FEI Tecnai F20 transmission electron microscope operated at 200 kV and powder X-ray diffractometer (XRD, Rigaku-D/max 2500 V). For ex-situ observations, these cells were disassembled from the coin-type cells after discharge–charge testings, CuO electrodes were peeled off, washed with ethanol and acetone, dried in air.

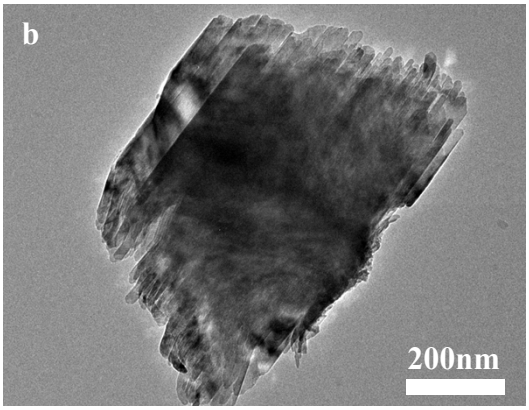

Figure S1 SEM and TEM images of the as-synthesized pristine CuO microsheets.

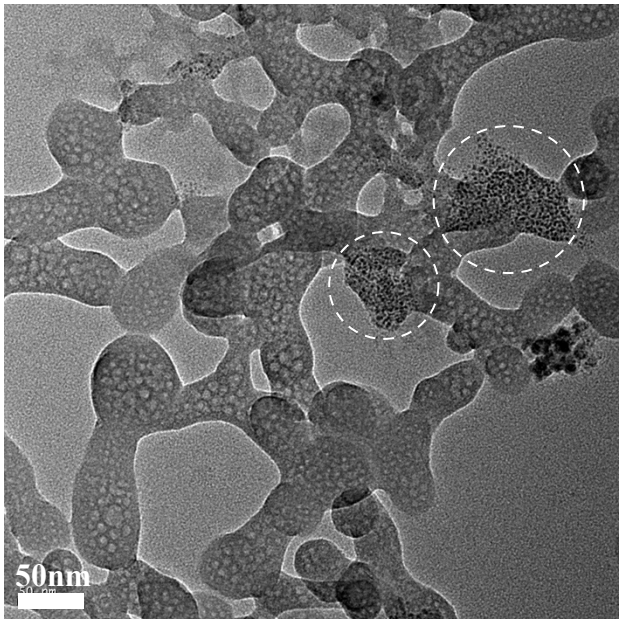

Figure S2. TEM image of CuO/Cu integrated electrode at the potential value of 1.6 V during charge process. The dot circles show Cu_2O nanoparticles.

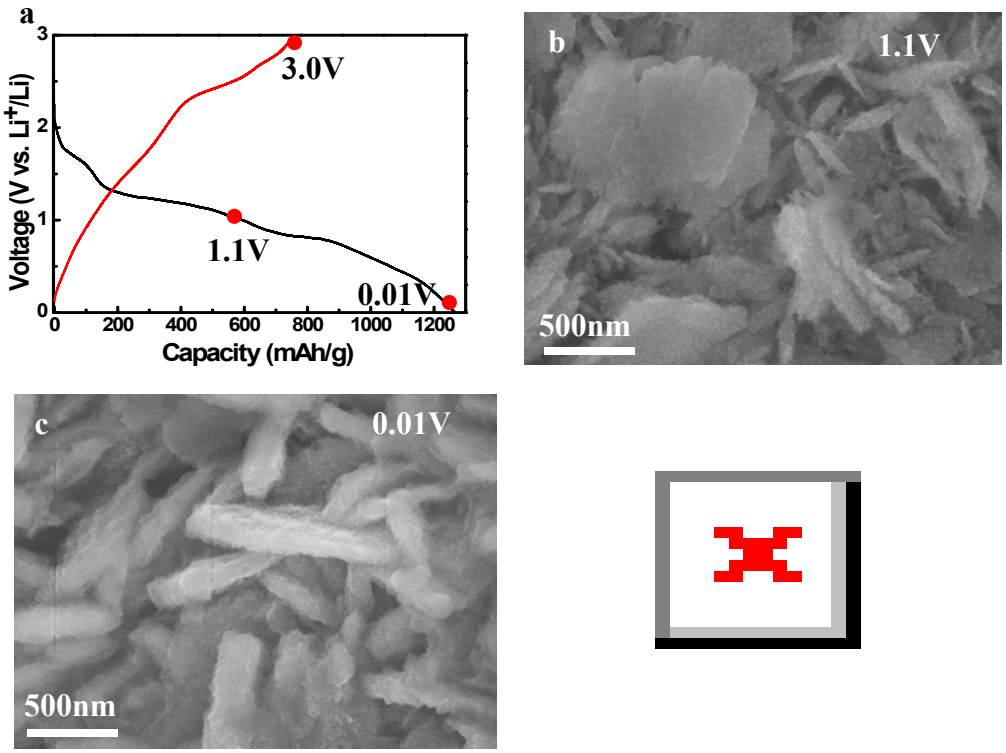

Figure S3. Charging/discharging curves at the potential window of 0.01-3.0 V. Red dots show three different charging and discharging states of CuO anode, which correspond to SEM images in b-d. SEM images of CuO/Cu integrated electrode during the first charge/discharge cycle. Discharge process: 1.1 and 0.01 V. Charge process: 3.0 V.