Electronic supplementary information for

Conversion Mechanism of CuO Nanowires during Lithiation/Delithiation as Revealed by in situ Transmission Electron Microscopy

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1. Experimental

Synthesis of CuO nanowires: In a typical procedure a copper foil was cleaned in an aqueous 1.0 M HCl solution for 30 min, followed by rinsing with distilled water for several times. After drying by using N_2 gas it was then placed in a furnace and immediately heated at 500 °C for 3 hours in an oxygen atmosphere.

Characterization. X-ray powder diffraction (XRD) patterns were recorded on a Philips X´Pert PRO MPD X-ray diffractometer operated at 35 kV and 45 mA with Cu Kα radiation. Transmission electron microscopy (TEM) images were taken on a JEOL JEM-3000F transmission electron microscope with an accelerating voltage of 300 kV.

Construction of the CuO nanowire based LIBs:

In situ transmission electron microscopy (TEM) observations were conducted in a JEOL-3100 FEF equipped with an Omega filter and a Nanofactory Instruments STM-TEM holder. In order to build up the test cell, an individual CuO nanowire was attached to the gold rod, which was further attached to the piezo-manipulator. A small piece of lithium foil was also attached to another gold rod as a reference and counter electrode. Anionic liquid electrolyte (ILE) was prepared in advance by dispersion of lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) into N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP13TFSI). Before holder insertion into the TEM a drop of the ILE was placed on the surface of metal lithium tip. During our experiments, the CuO nanowires were loaded onto the edge of a gold rod with a freshly cut tip, by simply scratching the rod against bulk powders of CuO nanowires. There would be many CuO attached and protruding out of the edge. Because the opposite tip coated with Li and ionic liquid was in the micrometer scale. It was easy to choose an isolated CuO nanowires, and no complicated techniques were necessary. The lithiation was carried out at a negative bias in the range of -3V to 0V with respect to the Li metal. The experimental phenomena are similar but with quite different reaction rate, e.g., the lithiation rate at -3V is obviously faster than that of -2V and 0V. The delithiation processes of this nano-LIB cell were realized by applying a voltage of 3V on the CuO electrode versus the Li counter electrode.

2. Supporting Figures Information.

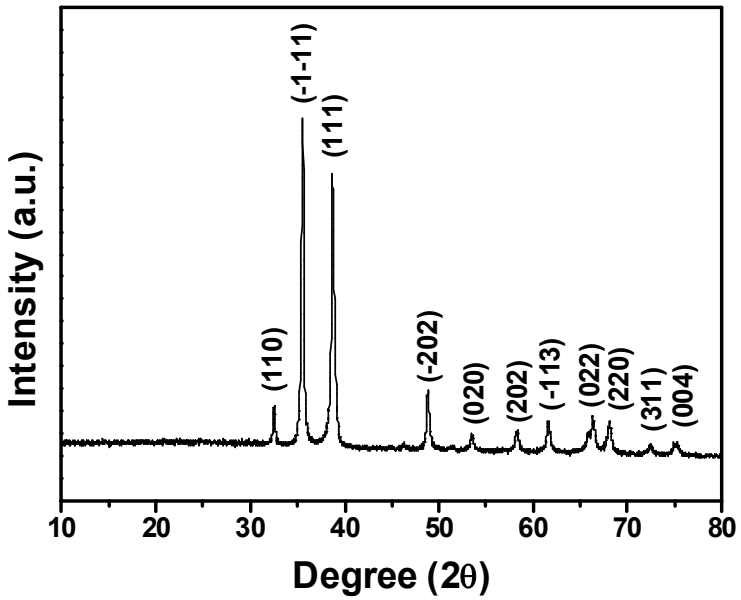

Fig. S1. XRD pattern of the obtained CuO nanowires.

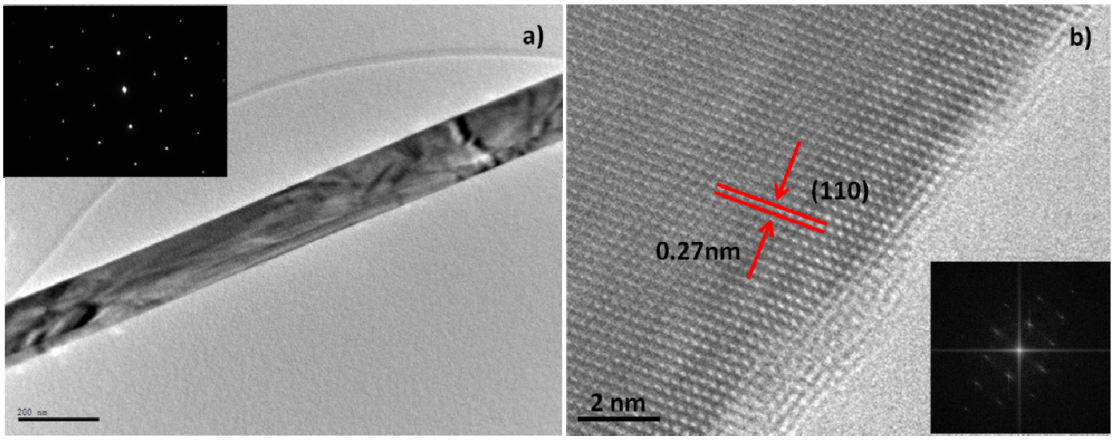

Fig. S2. a) TEM image of an individual CuO nanowire and its corresponding SAED pattern (inset); b) HRTEM image; the inset is the corresponding FFT pattern.

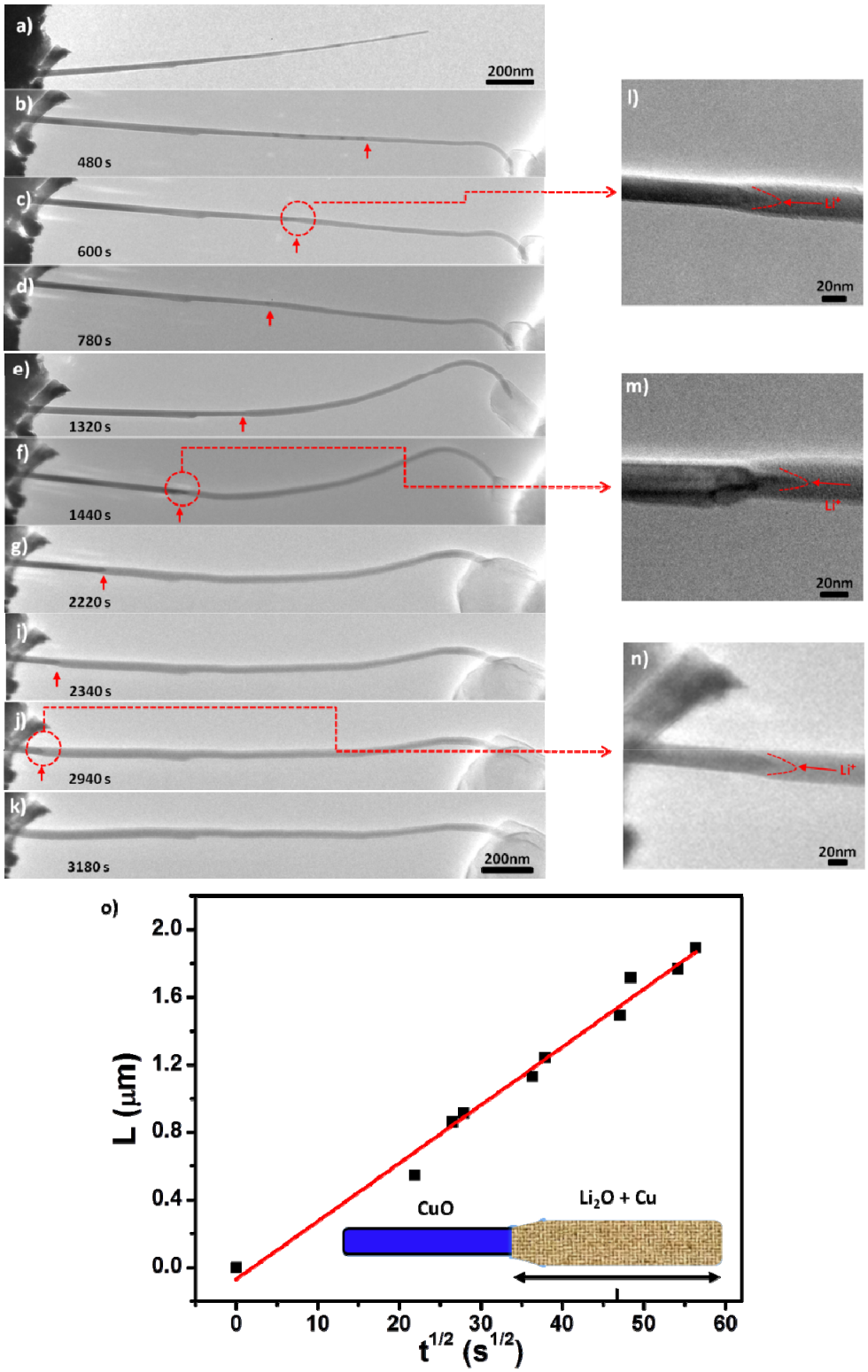

Fig. S3. a-k) Time-dependent morphology evolution of a CuO nanowire during the 1st Li-insertion process. i-n) Larger magnification TEM image showing the reaction front (marked with red arrows). o) Plot of the reaction front migration distance *L versus* time *t*.

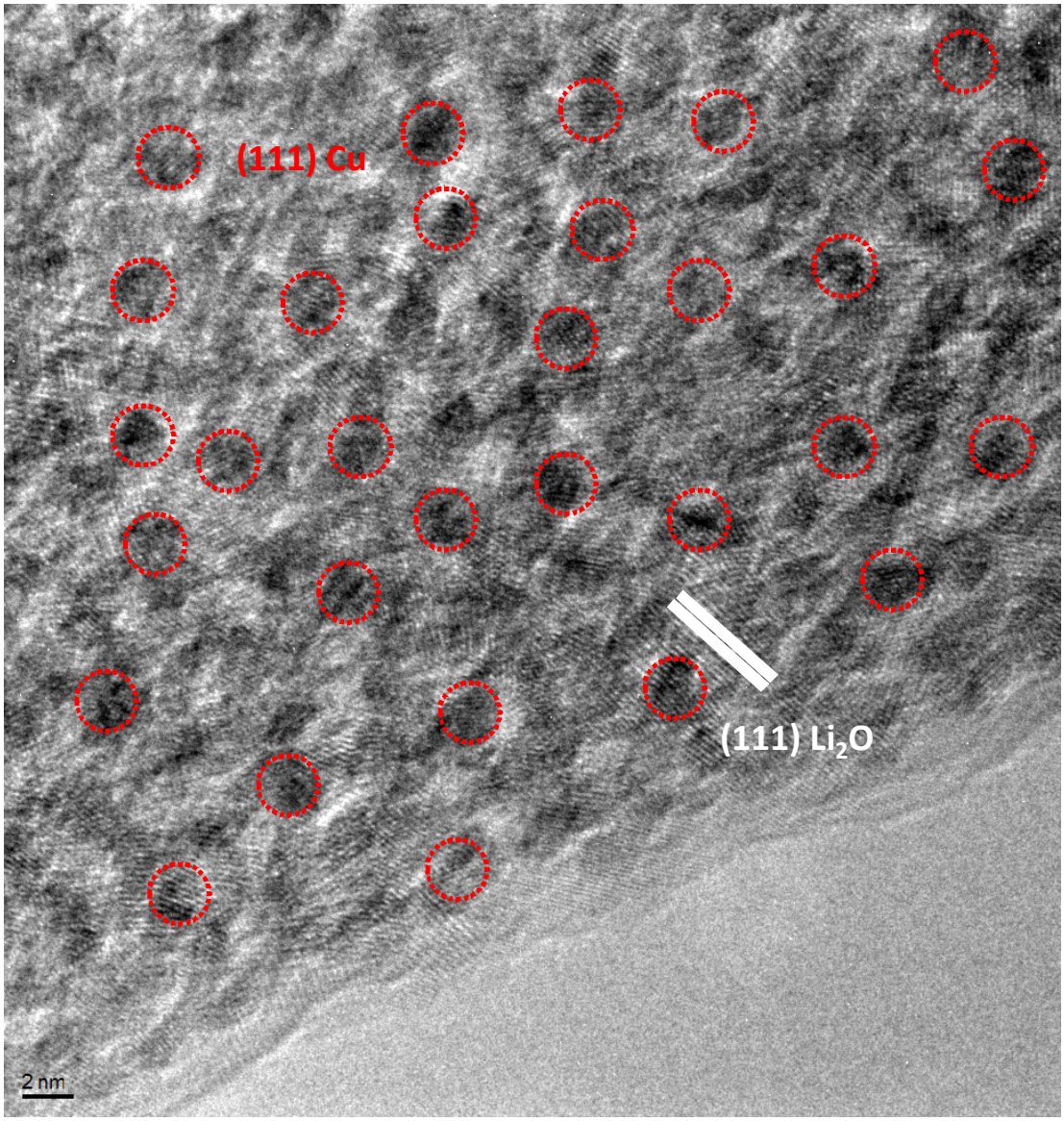

Fig. S4. HRTEM image taken from the framed area in Figure 2b. The red circle denotes the Cu nanoparticles.

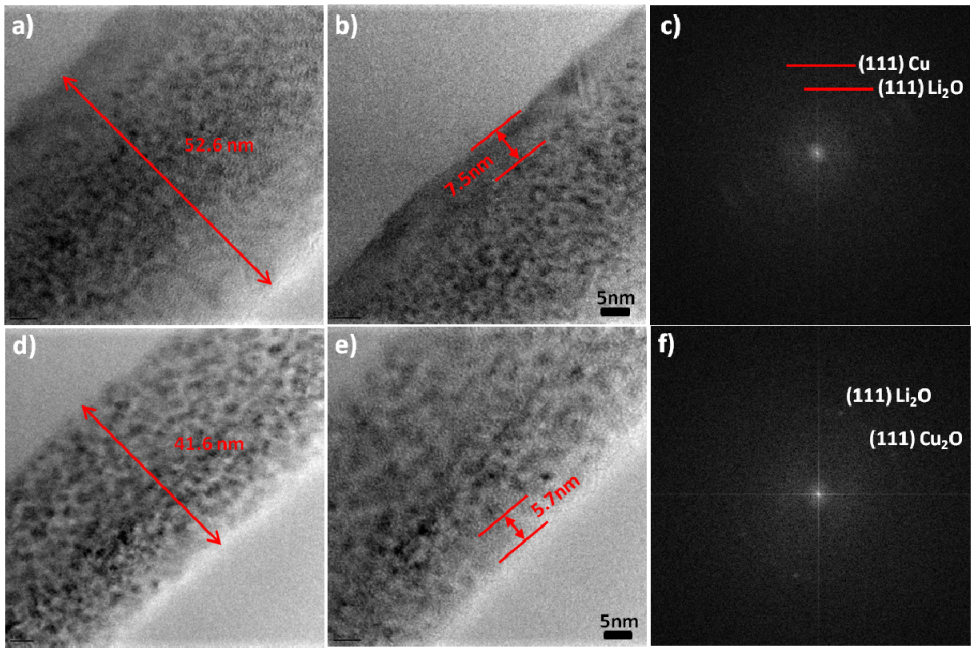

Fig. S5 Morphology changes and FFT patterns of a NW during the 2nd cycle at its different stages: a-c) 2nd Li-insertion, d-f) 2nd Li-extraction.

3. Supporting Movies Information.

Movie S1. An *in-situ* TEM movie showing the structural evolution of a CuO NW anode during the 1st lithiation process. As the reaction front moved, the original CuO nanowire diameter expanded and its length increased.

Movie S2. An *in situ* TEM movie showing the reaction front. Note that the reaction front always keeps conical shape during the whole process.

Movie S3. An *in situ* TEM movie depicting the 1st delithiation process of the CuO NW when applying an operation voltage of 3 V *vs* metallic lithium.