

Electronic Supplementary Information

***In-Situ* Chemical Mapping of Lithium-ion Battery Using Full-field Hard X-ray Spectroscopic Imaging**

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Materials and Electrochemical measurements

CuO powder (Aldrich) mixed with acetylene black and polyvinylidene fluoride (PVDF) with a weight ratio of 50:35:15 in N-methyl-2-pyrrolidone (NMP) solvent to produce the slurry. The resultant slurry, pasted on commercial carbon paper, was dried at 100 °C under vacuum for 24 h to form the working electrode. The coin cells (2032) with Kapton windows were then assembled in a high purity argon-filled glove box using lithium metal as the counter electrode and 1 M LiPF₆ (dissolved in a solvent consisting of 50% ethylene carbonate and 50% dimethyl carbonate by volume) as the electrolyte.

In Situ TXM study

The transmission x-ray microscopy imaging with hard x-ray was conducted at beamline X8C, NSLS, BNL. A field of view of $40 \times 40 \mu\text{m}^2$ with a $2\text{k} \times 2\text{k}$ CCD camera was used. Three types of imaging were carried out. First, *in situ* TXM imaging was conducted on the assembled CuO battery coin cell during lithiation/delithiation. The lithiation-delithiation process was conducted by cyclic voltamograms (CV) measurements, which were performed on an electrochemical workstation (Potentiostat/Galvanostat/EIS (VMP3)) over the potential range of 0.05–3.0 V (vs. Li⁺/Li) at a scanning rate of 0.15 mV s^{-1} at room temperature. The *in situ* TXM imaging was used to image the morphological evolution of the CuO particles during the electrochemical reaction. Each image was collected with 10 s exposure time with 2×2 binned camera pixels at x-ray energy of 9040 eV. In order to minimize possible radiation damage on the sample, different imaging rate was chosen with variations between 5 to 30 minutes per image, depending on the voltage. At voltage where significant morphological evolution may occur due to expected reduction-oxidation reaction, faster image rate was used. The total x-ray dose was thus reduced to minimize possible x-ray beam damage to the sample. Secondly, before and after each half cycle (one full lithiation or delithiation), a mosaic imaging mode of 11×11 images with $40 \mu\text{m}$ field of view for each was used to collect an image with effectively larger field of view ($440 \times 440 \mu\text{m}^2$) on the sample to ensure that the observed morphological evolution was indeed universal within the sample, rather than was locally caused by x-ray beam. Each single image was collected with 1 s exposure time with x-ray energy of 9040 eV. 4×4 camera pixels were binned into one output image pixel. Third, to study the chemical state evolution, a full X-ray Absorption Near Edge Structure (XANES) image series was also collected on the fresh cell and also on the same location within the cell after each half cycle. Each XANES image series was measured by scanning Cu absorption K-edge from 8960 to 9840 eV, with 2 eV step size, and one TXM image at one energy step, which generate $1\text{k} \times 1\text{k}$ XANES spectra with 2×2 binned pixels. Each image was collected with 10 s exposure time. 2×2 camera pixels were binned into one output image pixel.

Other physical characterization

In situ synchrotron XRD patterns were performed on the same sample as the one for the TXM experiment during lithiation-delithiation process at X14A beamline at NSLS. Scanning electron microscopy (SEM) imaging was carried out using a Hitachi S-4800 microscope with an operation voltage of 5 kV. High-resolution transmission electron microscopy and electron diffraction were carried out using the JEM-3000F microscope operated at 300 kV. These electron microscopy experiments were done at Center for Functional Nanomaterials at BNL.

XANES Data Analysis

All the XANES data analysis was carried out using customized program (MatLab, MathWorks, R2011b) developed in house (beamline X8C group, NSLS, BNL). Background normalization was carried first out for TXM images, with a unique background image collected at every energy. With all 1024×1024 pixels, we can extract the full spectrum (x-ray intensity v.s. energy) for each pixel. Based on Beer's Law, the attenuation of x-ray from a given phase with attenuation coefficient μ and thickness t can be written as:

$$\frac{I}{I_0} = \exp(-\mu(E)t) = \exp(-\mu_{Cu}t_{Cu}) \cdot \exp(-\mu_{Cu_2O}t_{Cu_2O}) \cdot \exp(-\mu_{CuO}t_{CuO}),$$

where I_0 is the incident x-ray intensity and I is the x-ray intensity after the attenuating phase. Notice that μ is a function of energy and can be attributed to three possible phases: Cu, C_2O and CuO.

The scaled $-\ln(I/I_0)$ at each of the 1024×1024 pixels was then fitted with the linear combination of three μ values. The ratio of the weighting factor is an analogy of the thickness fraction and therefore represents their volume fraction.

$$-\ln\left(\frac{I}{I_0}\right) = \mu_{Cu}t_{Cu} + \mu_{Cu_2O}t_{Cu_2O} + \mu_{CuO}t_{CuO}.$$

The pixels which do not show significant contrast change before and after the Cu edge (indicating that there are no Cu in those pixels) can be easily excluded through a filtering process.

The fitting was carried out by calculating the R value for each spectrum (for each pixel), which is defined as:

$$R = \frac{\sum_{E=E_i}^{E=E_f} (data_E - ref_E)^2}{\sum_{E=E_i}^{E=E_f} data_E^2},$$

where E_i is 8060 eV, E_f is 9040 eV, $data_E$ is the $-\ln(I/I_0)$ value for the given pixel at energy E , the ref_E is the possible fitting reference $-\ln(I/I_0)$ value, a linear combination of Cu, C_2O and CuO. We considered all possible combination with Cu, Cu_2O and CuO by 5 vol. % resolution, which resulted in a total 231 possible combinations. For a given pixel with its associated spectrum), the smallest R was determined to find a best-matched phase combination of Cu, Cu_2O and CuO that can be assigned to the specific pixel.

The standard XANES spectra for the reference materials Cu (99.9995%, Aldrich), Cu_2O (99.99%, Sigma-Aldrich) and CuO (99.995%, Aldrich) were measured at the TXM beamline X8C (NSLS, BNL) and verified at a standard XANES beamline X19A (NSLS, BNL). The TXM XANES imaging on the reference materials was carried out by using the same condition as used in the XANES imaging for the copper oxide battery cell sample.

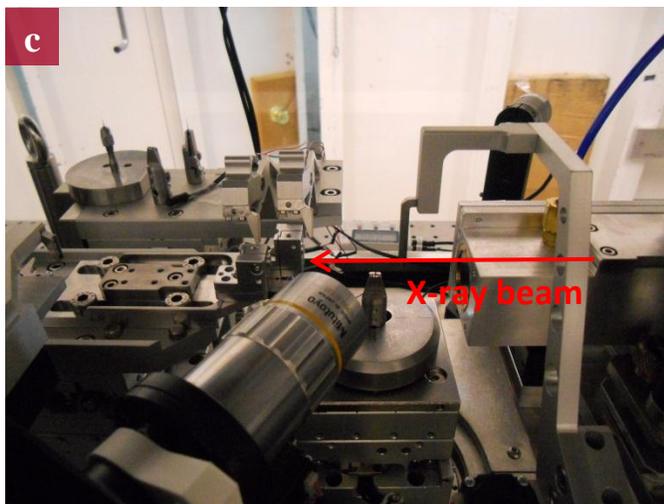
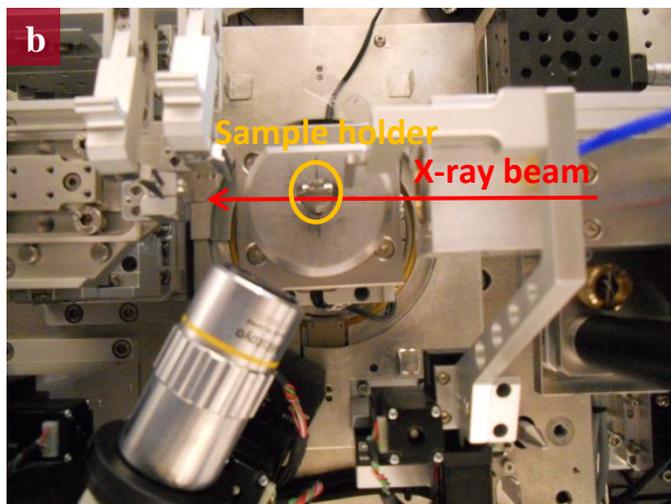
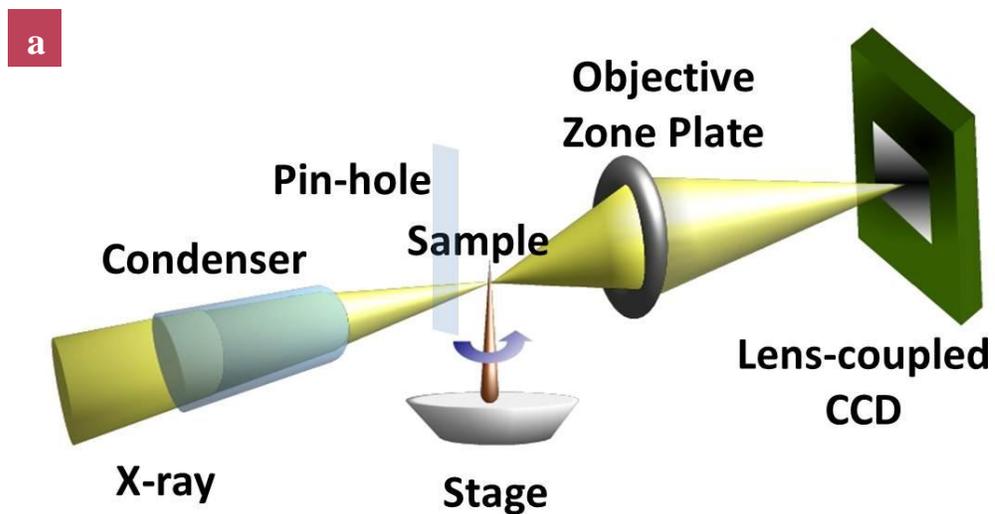


Fig. S1. 3D transmission X-ray microscopy setup at beamline X8C at NSLS.

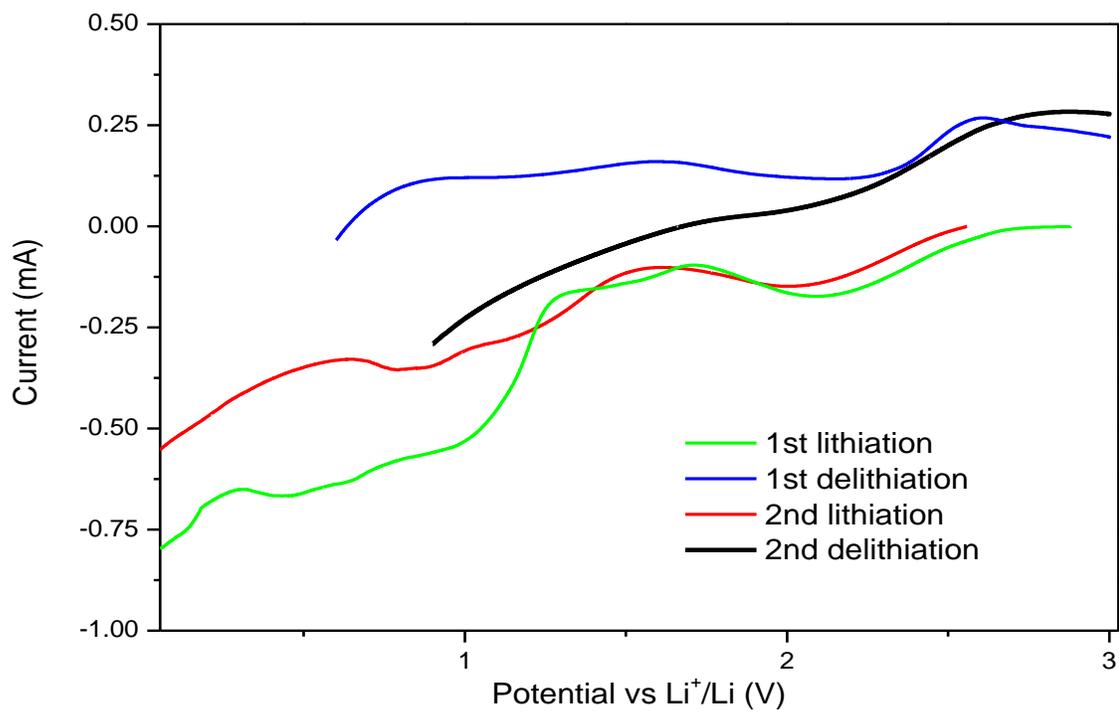


Fig. S2. Cyclic voltammetry curves during the first two cycles at different potentials for CuO electrode

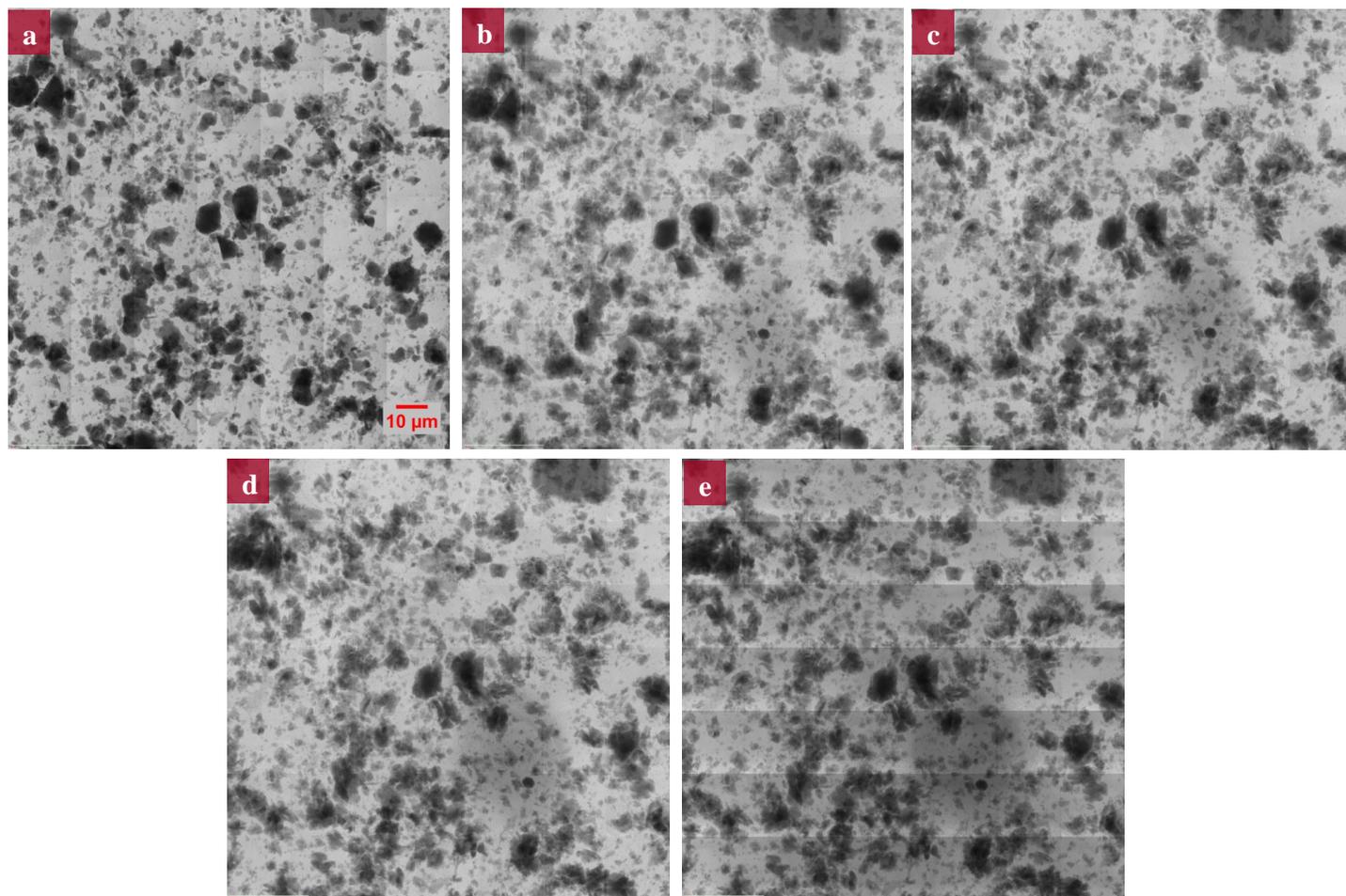


Fig. S3. The mosaic micrographs of CuO anode in lithium-ion batteries during cycling. (a) fresh sample; (b) 1st lithiation; (c) 1st delithiation; (d) 2nd lithiation; (e) 2nd delithiation.

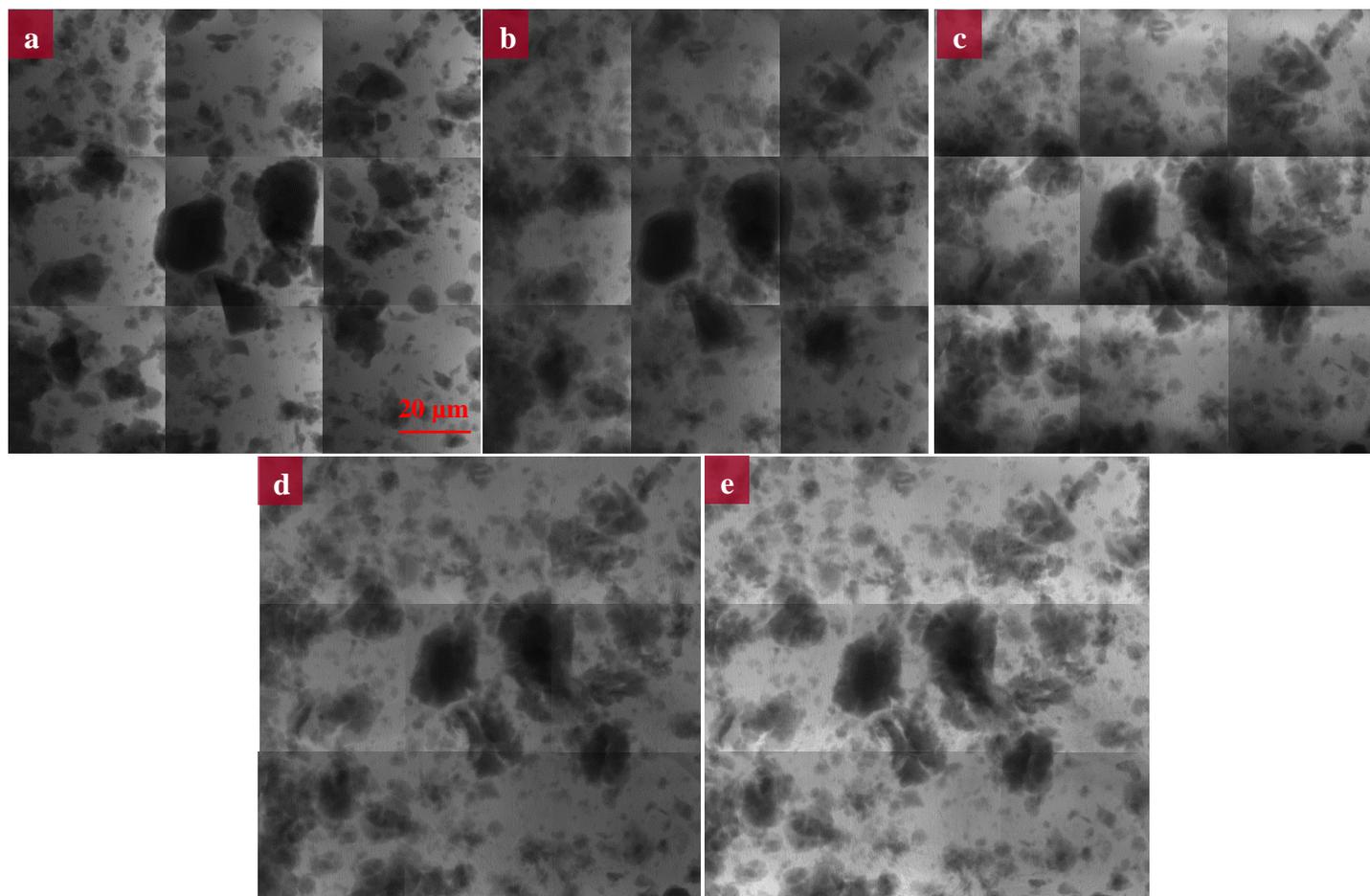


Fig. S4. The mosaic micrographs of CuO anode in lithium-ion batteries during cycling. (a) fresh sample; (b) 1st lithiation; (c) 1st delithiation; (d) 2nd lithiation; (e) 2nd delithiation.

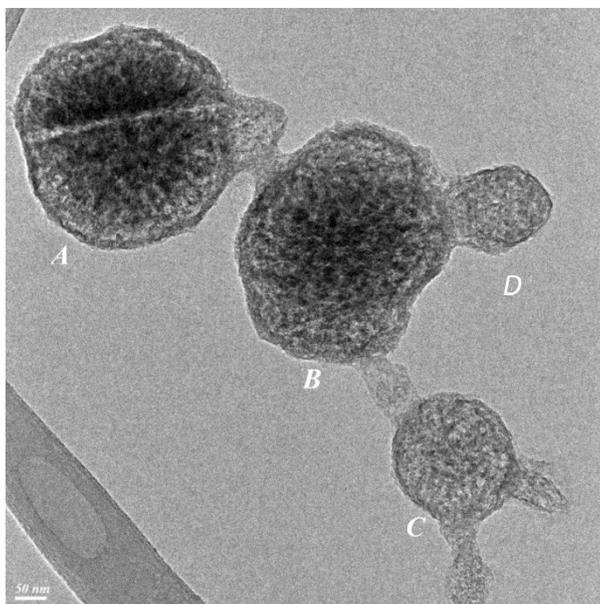


Fig. S5. Ex-situ HRTEM images of 1st lithiated - delithiated CuO

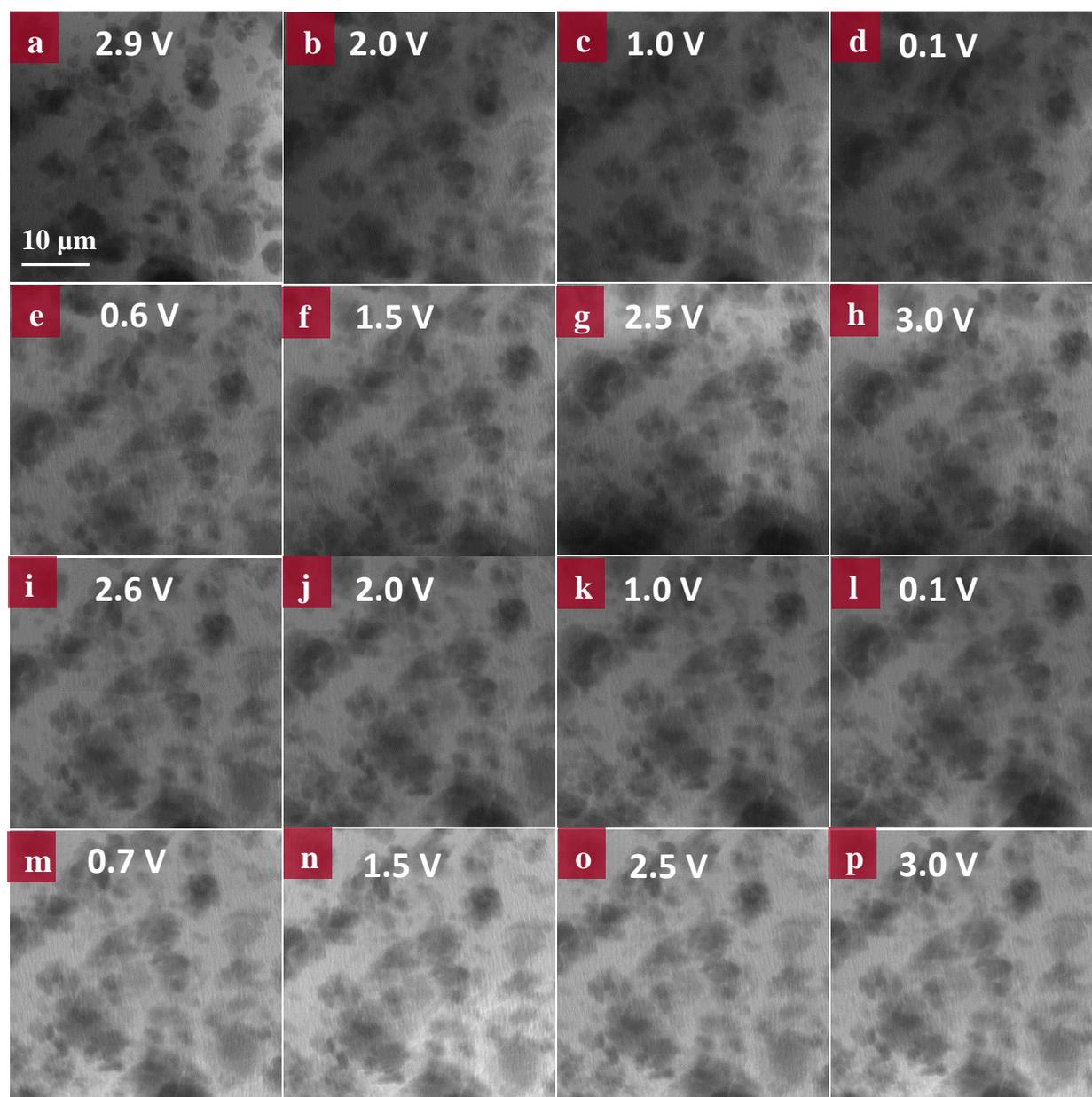


Fig. S6. Morphology evolution at different potentials for small CuO particles during the first two cycles

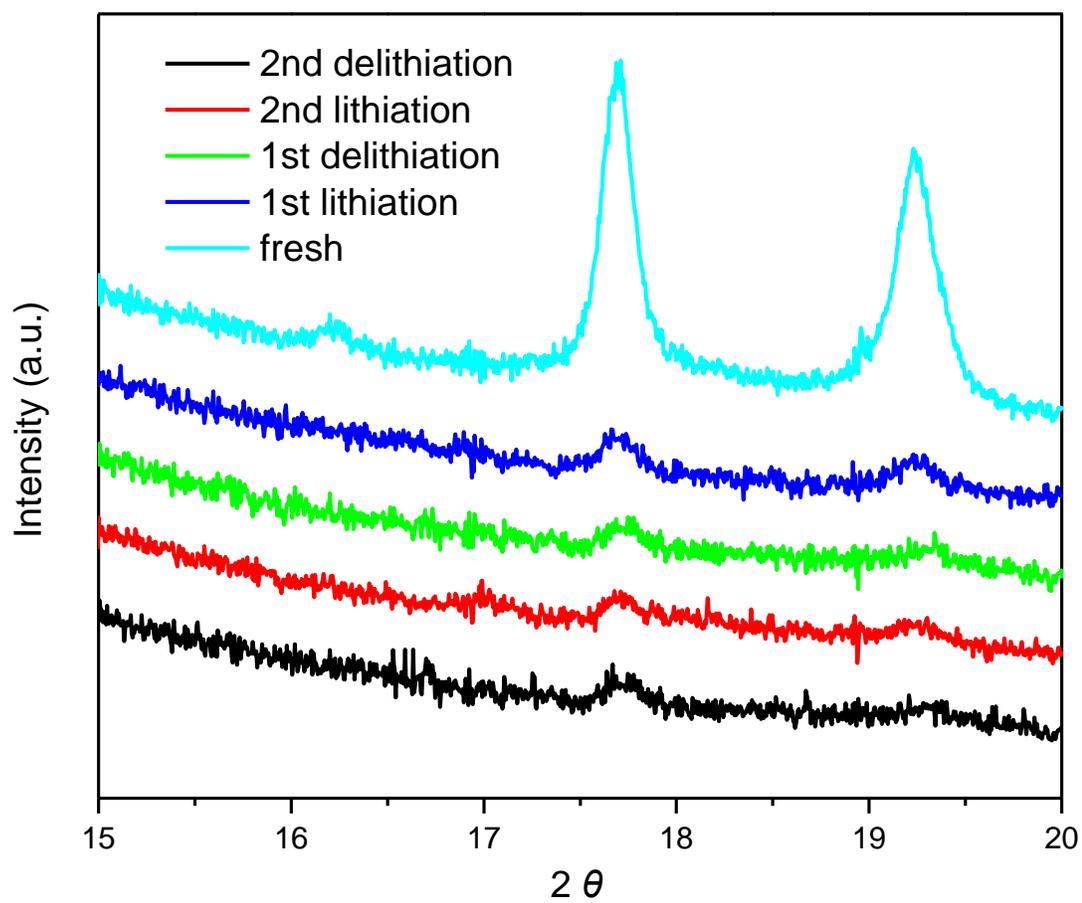


Fig. S7. synchrotron XRD patterns of CuO during the lithiation/delithiations.