Electronic Supplementary Material (ESI) for ChemComm.

Experimental Procedure

In situ XPS/AES cell preparation

The CuO nanoparticles purchased from Sigma-Aldrich (D <50 nm) were dispersed into ethylene glycol at 1.0% weight. The solution was drop cast onto a 400 mesh carbon (≈20 nm) coated titanium (Ted Pella, Inc.) and dried in an oven at 85^{o}C for 30 minutes. The *in situ* cell was assembled in the Ar-filled glove box (LABstar, MBRAUN) with oxygen and water concentration <0.5ppm. The grid supported CuO nanoparticles served as the anode, which rested on top of 10wt% LiTFSI in P_{13}TFSI soaked Whatman fiberglass separator, which was placed on a piece of lithium metal (1.5 mm in thickness) (Sigma-Aldrich). The lithium counter electrode was connected to the stainless steel current collector. A nickel coated bronze metal served as the contact to the working electrode. The cells were sealed in an air-tight jar prior to transfer to the XPS, AES or SEM chambers.

Electrochemical measurements

Cyclic voltammetry and potentiostatic charge and discharge were carried out by using a digital potentiostat (SP200, Biologic Co.) connected to the XPS, AES, or SEM systems.

XPS analysis

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a PHI 5400 spectrometer using Al Kα radiation ($h\upsilon = 1486.7$ eV). The instrument vacuum exceeded 5x10^{-8} Torr during the experiments. The spectrometer was calibrated with the photoemission lines of Ag 3d$_{5/2}$, Au 4f$_{7/2}$ and Cu 2p$_{3/2}$. The spectra were recorded in constant analyzer energy mode at a pass energy of 143.05 eV for survey spectra and 35.75 eV for high resolution spectra. The survey spectra were summed over 3 scans, and high resolution spectra were summed over 15 cycles. All spectra were energy calibrated using the hydrocarbon peak at the binding energy of 285.0 eV. The data was evaluated using the CasaXPS software, and the background subtraction applied to the high resolution scans followed the method according to Shirley. The experimental curves were fit using Gaussian-Lorentzian product functions; 70% Gaussian and 30% Lorentizian.

AES analysis

Auger electron spectroscopy (AES) measurements were carried out in an ultrahigh vacuum chamber with the PHI 660 scanning Auger microprobe. The vacuum pressure of the chamber remained at 4×10^{-8} Torr. Acquisitions were performed with a 5 keV primary electron beam over 25 cycles in the energy range from 30 to 1230 eV. To eliminate any influence of the electron beam on the sample, the spectra were acquired from different points on the sample after each voltage step. Auger data was analyzed by using Multipak software.

SEM analysis

SEM images were recorded with an FEI DB235 operating at 5 kV in a vacuum of 3×10^{-5} mbar. The images were required every 10 minutes during galvanic charging at a constant voltage of 0.1V.

Figure S1. Images of the *in situ* sample holder.

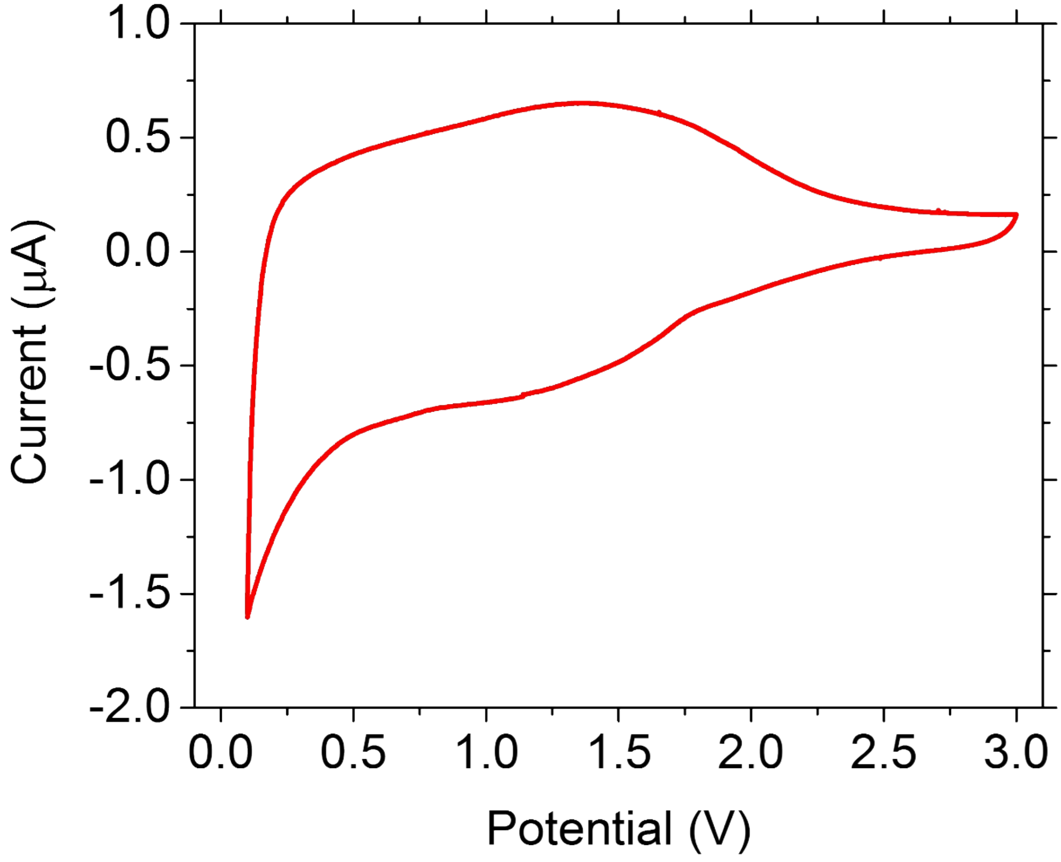

Figure S2. Cyclic voltammetry of CuO nanoparticle electrode measured *in situ* at a scan rate of 1mV/s.

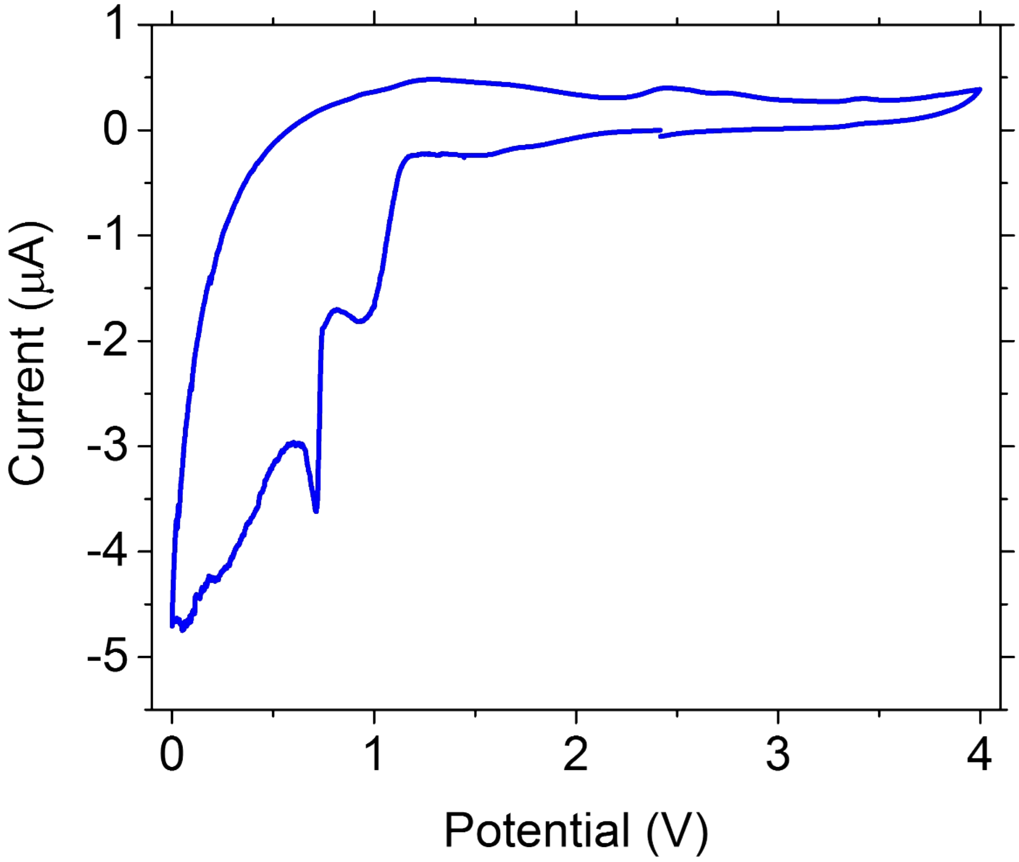

Figure S3. Cyclic voltammetry of high concentration CuO nanoparticle electrode measured *in situ* at a scan rate of 0.1mV/s.

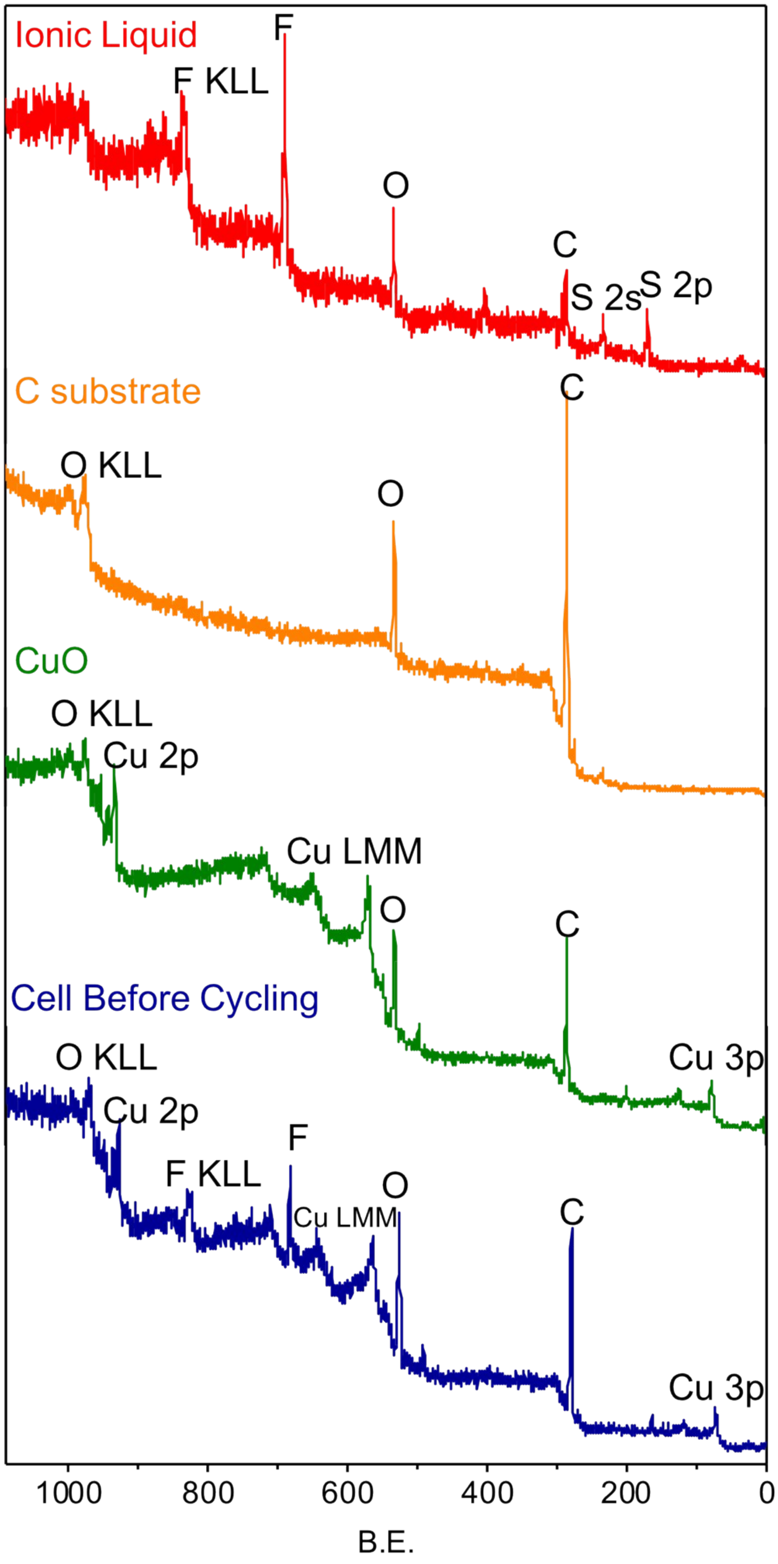

Figure S4. XPS survey scans of the electrolyte, C substrate, CuO, and the cell before cycling.

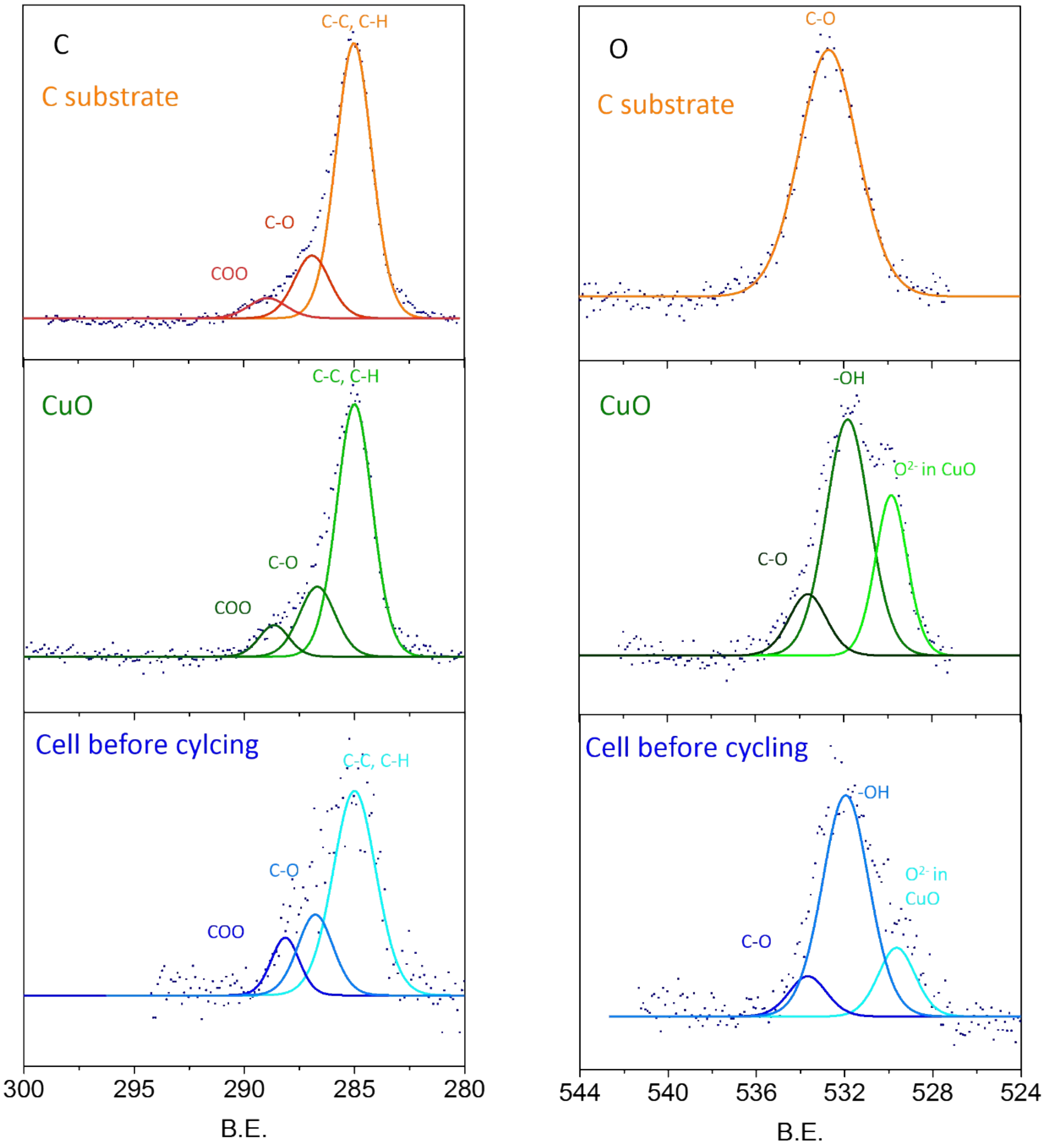

Figure S5. XPS analyses of the C 1s and O 1s core peaks performed onto the C substrate, CuO and the cell before cycling.

Potential (V vs Li/Li$^+$)	**Cu $2p_{3/2}$ B.E. (eV)**	**O 1s B.E. (eV)**
Before cycling	933.7 (Cu^{2+}) [ref. 26] Satellite: 943.7, 940.7	529.6 (O^{2-} in CuO) [ref. 24] 533.6 (C-O) [ref. 24] 532.2 (OH$^-$) [ref. 27]
1.2V	933.1 (Cu$^+$)	529.6 (O^{2-} in CuO) 532.2 (OH$^-$)
0.1V	931.4 (Cu^0) [ref. 29]	531.2 (O^{2-} in Li$_2$O) [ref. 28]
4.5V	931.9 (Cu$^+$) [ref. 29]	529.5 (O^{2-} in CuO) 531.2 (O^{2-} in Li$_2$O)

Table SI. XPS Binding Energies (B.E.) of Core Peaks for Cu $2p_{3/2}$ and O 1s.