Materials and Methods

A Poseidon TEM holder comprised of a microfluidic cell was developed by Protochips Inc and is described by Klein *et al* (Klein, et al., 2011). A Harvard Apparatus Pico Pump Plus syringe pump flows liquid through polyether ether ketone (PEEK) tubing into the back of the TEM holder. The fluid flows through internal tubing from the back of the holder to the tip of the holder, which houses the microfluidic cell. The cell as shown in Fig S1 is comprised of two silicon-based chips separated 0.15 μm to 0.50 μm apart by either a gold or SU-8 (an epoxy-based negative photoresist) spacer. Liquid flows through the separated chips, out through the internal plumbing of the holder and eventually into a waste beaker. The microfluidic cell is enclosed onto the tip of the holder by a plate that is screwed into the body of the holder. O-rings are installed at the bottom of the holder and on the plate, enabling liquid to flow through the chips and around the edges of the chips but not into the vacuum of the microscope.

The silicon chips are coated in 50 nm of low-stress silicon nitride and the silicon is back-etched in the center of the chips to form the electron-transparent viewing windows, which are 10-50 μm wide by 200 μm long. On one of the chips, an additional SU-8 or gold layer is deposited, ranging from 0.15 μm to 0.50 μm thick, which separates the chips enabling a layer for liquid to flow. Before the chips are loaded into the holder, they are first cleaned with acetone (99.5% purity, Mallinckrodt chemicals) and ethanol (100% purity, Koptec-DLI chemicals) to remove any remaining photoresist and debris, followed by 1-3 minutes of plasma cleaning to make the surface hydrophilic. If nanoparticles were

to be imaged, 0.5 μL of dispersed nanoparticles were pipetted onto the chip that would be loaded on the top and allowed to dry.

The microfluidic cell was assembled by inserting one of the two chips, then depositing a 0.5 μL drop of liquid directly on the first chip and then loading the top chip. The top plate was then screwed on to fully assemble the cell. Further liquid was then flown in at a rate of 100-300 μL/h through the 360 μm diameter PEEK tubing. The small diameter of PEEK tubing is used to minimize vibrations coupled into the microscope. The holder is checked for leaks using the vacuum gauge on the plasma cleaner and loaded into the microscope, where the pressure is monitored for leaks.

Liquids prepared for the EELS measurements comprised of propylene carbonate (99%, Fisher Scientific), 10 mM copper sulfate (99.99% anhydrous, Sigma-Aldrich) in aqueous solution, and ethylene glycol (99.5%, Mallinckrodt chemicals). All aqueous solutions are made with ultra-pure Millipore water (18.2 MΩ/cm) unless otherwise indicated. 30 nm spherical diameter gold nanoparticles (NanoPartz) were used for resolution testing.

For the EFTEM session, a Poseidon Electrochemical Protochips holder was used, with three electrical contacts in the microfluidic cell of the holder. For the EFTEM data shown, no electrochemical activity had occurred, so the electrochemical capability of the cell was not used. The $LiFePO_4$ nanoparticles were deposited onto the working electrode, which is on the entrance SiN_x membrane (although ideally for TEM it would be on the exit membrane). $LiFePO_4$ was synthesized by a solid-state reaction (Kang & Ceder, 2009). Specifically, a mixture of Li_2CO_3, $FeC_2O_4 \cdot 2H_2O$ and $NH_4H_2PO_4$ (molar ratio: Li/Fe/P=1/0.9/0.95) was ball-milled for 2 hours under argon using a Spex8000 mixer. The ball-milled precursor was first heated at 350 ºC for 10 hours under argon. After

cooling down, the precursor was ground in a mortar and then heated at 600 ºC for 10 hours under argon to get the final product.

Imaging and EELS were performed using a monochromated FEI Tecnai F-20 STEM/TEM operated at 200 kV and equipped with a Gatan 865 HR-GIF spectrometer for EELS analysis. While the monochromator was not employed here, the study did benefit from the system's improved energy stability. A high-angle annular dark field detector provided an incoherent projection image of the specimen with a signal intensity proportional to the amount of material and its atomic number, which is also known as 'Z-contrast'. The HAADF-STEM imaging under such conditions normally has a typical beam dose of 10 pA. EELS were acquired with a dispersion of 0.2 – 0.5 eV/px, with energy resolution of three channels. The convergence and collection angles for STEM EELS were 9-10 mrad and 20-30 mrad, respectively. EELS was aligned and diffraction shift values noted for a crystalline or nanoparticle sample before the liquid cell was loaded to ensure the correct alignment of EELS even when the thickness of the liquid made aligning the beam into the spectrometer impractical. EFTEM was performed with an energy slit of 5 eV, with acquisition times of 3 seconds, also aligned on a crystalline or nanoparticle sample to 2 eV resolution. Since the energy slit was narrow, chromatic blur did not limit our spatial resolution, and we did not find it necessary to use an objective aperture in EFTEM mode.

All optical ultraviolet-visible (UV/VIS) absorption spectra were obtained using a HP 8453 diode array spectrometer at room temperature in denoted solvents, with a conventional 1.0 cm quartz cell.

Deconvolution

Fourier Log deconvolution is a commonly used method to remove multiple scattering signal from your EELS signal. (Egerton, 1986) Here we have deconvolved the spectra using Egerton's FLogS code, which is capable of handling thick samples ($\pi < t/\lambda < 10$).(Egerton, 1986) The O-K edge from the thinnest liquid layer (284 nm) is resolved as shown in Fig. S2 (a), and deconvolution helps define the peak from the background. In thicker liquid layers where the peak is obscured, deconvolution cannot extract the signal, and generates ringing artifacts as shown in Fig. S2 (b) for a 352 nm thick layer.

References

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KANG, B. & CEDER, G. (2009). Battery materials for ultrafast charging and discharging. Nature **458**(7235), 190-193.

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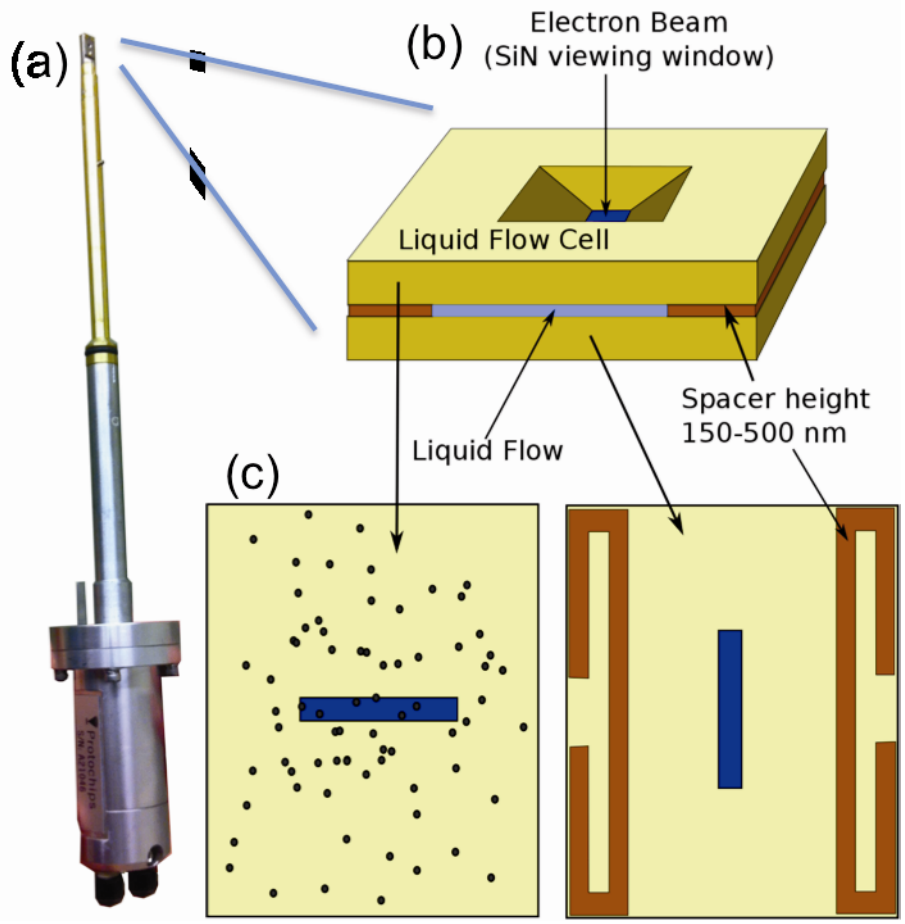

Figure S1. The Protochips liquid cell holder is shown in (a), which houses a microfluidic cell, consisting of two chips separated by a spacer, as shown in (b). The two chips are assembled with the windows orthogonal to each other, as shown in (c), with nanoparticles on the entrance (top) surface for STEM.

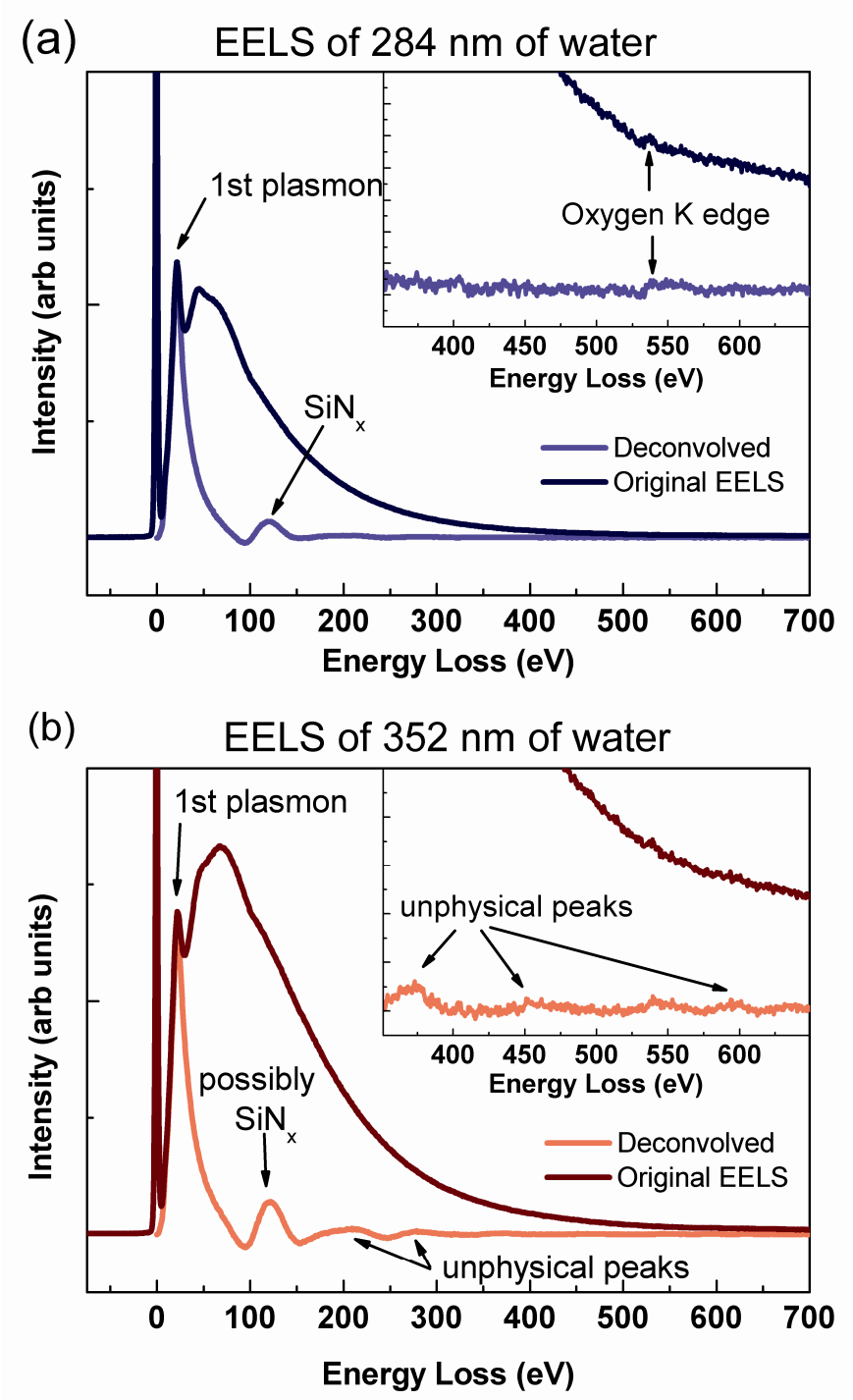

Figure S2. The O-K edge extracted through (a) 284 nm and (b) 352 nm of water by Fourier-Log deconvolution. We can resolve the O-K edge through the thinnest layer where the O-K edge is present above the background level, but due to ringing artifacts we cannot resolve the O-K edge through thicker layers where the signal is already obscured.

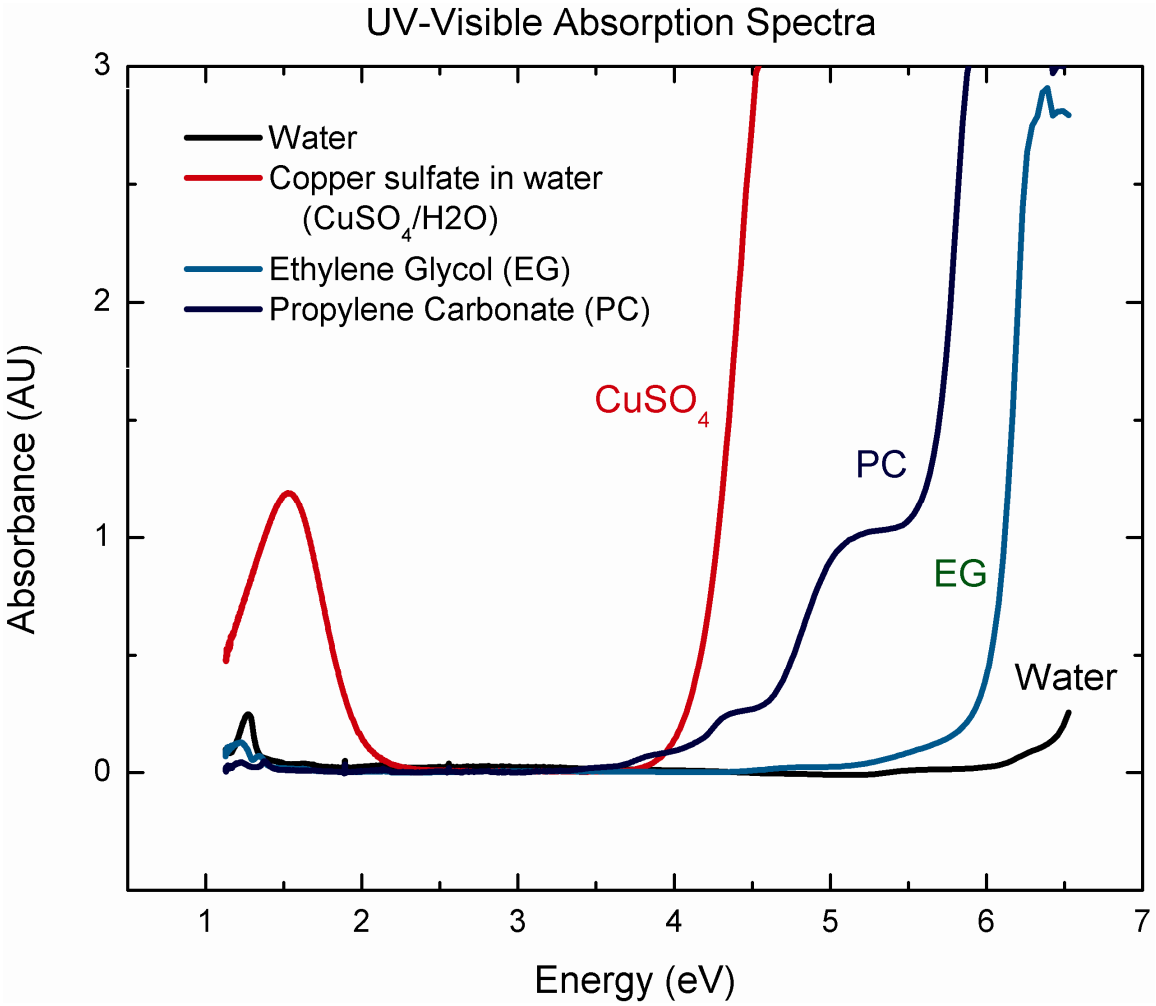

Figure S3. UV-VIS spectroscopy of water, propylene carbonate, ethylene glycol, and 10 mM copper sulfate/water. The cutoff corresponding to the optical gap of the liquid is defined where the absorption rises to 1 AU.