

Observing Nano-Scale Dynamics of Active Soft Materials by *In Situ* Electrochemistry and Liquid Cell Transmission Electron Microscopy

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Systems such as microtubules and actin fibers are inspiring examples of fuel-driven dissipative supramolecular assemblies [1]. Their complex and dynamic characteristics serve as the basis for biological response to environmental pressures and fundamental biological processes [2-3]. These systems are far from equilibrium as they require continuous fuel to maintain their function [4]. If changes in the supply of fuel occur, then the system adapts by establishing a new non-equilibrium steady state which may be characterized on a structure growth reduction continuum.⁵ Adaptability such as this is one such characteristic that researchers have designed into synthetic dissipative assemblies using many different chemical fuel sources [4, 6-17]. Though multiple chemically fueled out-of-equilibrium systems have been designed successfully, electrically fueled dissipative systems are absent from literature.

I work in collaboration with the Guan lab to probe the electrochemical fueled dissipative self-assembly of a polymer system they have developed. The LP-TEM technique provides nanometer spatial resolution and sub 0.1 second temporal resolution which makes it a optimal technique to look at macromolecular self-assembly. In this dissipative system, self-assembly is fueled by the electrochemical oxidation of ferrocyanide Fe^{II} to ferricyanide Fe^{III} . Two Fe^{III} molecules then go on to oxidize two thiol (CS-H) bonds to a disulfide (CS-SC) bond. The CS-SC molecule then forms multi-micrometer long fibers via non-covalent interactions between CS-SC molecules. Driving disassembly of these fibers is a reductant that reduces the CS-SC bond to two CS-H bonds. Due to the competing rates of assembly and disassembly the fibers are dynamic in their growth and degradation. Important knowledge to be gained is what mechanism the fibers begin to form at early timepoints and what local conditions promotes fiber disassembly which the electrochemical liquid phase transmission electron microscopy (E-LPTEM) is optimal for studying these dynamic processes.

Here we show the growth and dissipation of this redox active material as well as the modification of already formed material using the E-LPTEM technique. Furthermore, we show the application of the dissimilarity index to the LPTEM images as a way to highlight the area of dynamic growth/deformation.

A DENs solutions Stream liquid cell TEM holder that utilizes a silica nitride liquid cell. The bottom chip has platinum working, pseudo-reference, and counter electrodes deposited on its surface for in situ electrochemical measurements. When working with a low z value material that is also redox active special care must be taken to find an acceptable beam intensity to minimize beam sample interactions. Figure 1 is a time panel showing the CSH system being imaged at different beam intensities. At dose rates above $1 \text{ e } \text{\AA}^{-2} \text{ s}^{-1}$ beam induced products are formed. At high rates of $10 \text{ e } \text{\AA}^{-2} \text{ s}^{-1}$ an interesting cube morphology is formed. Beam induced product formation can also be verified using post-mortem scanning electron microscopy (SEM). This is due to these products being deposited on the surface of the silica nitride chip in a circle corresponding with the beam diameter. These deposits and not easily

rinsed off the chip. All other particle formations are easily rinsed from the surface of the chips. At dose rates equal or below $1 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$ little beam induced product is seen during TEM imaging and verified using post-mortem SEM imaging. Electrochemical stimulated growth is shown in the time panel below (figure 2). During imaging, current was passed for 40 seconds and stopped while continuing to image. During the initial 40 seconds particle growth is seen. After the passage of current is finished the particles remain but then slowly disassemble. In situ imaging of electrochemical modification of preformed assemblies is also demonstrated in figure 3. Here the dissimilarity index is used to highlight propagating waves of growth and disassembly corresponding with a chronopotentiometry input. These waves closely correspond to the working electrode topology to include the electrode in the imaging area as well as electrode features outside of the imaging area. This shows that growth or modification of assemblies can be done with spatial and temporal control.

Using a combination of dose studies and in situ electrochemical formation of redox active material we have shown that acceptable deconvolution of electron beam interactions and electrochemical assembly can be accomplished. With this successful deconvolution along with improved imaging analysis to highlight dynamic behavior we have demonstrated that E-LPTEM can be used to study active materials and provide insight into their assembly-disassembly kinetics and spatio-temporal dynamics.

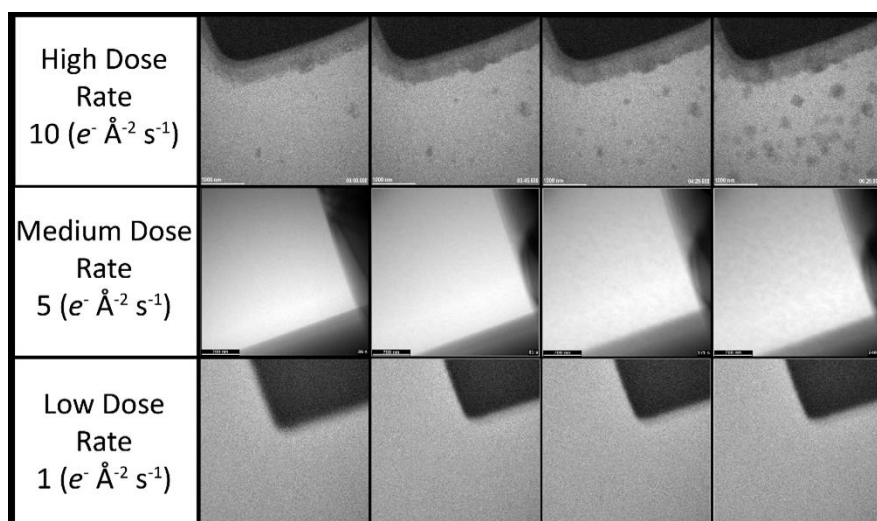


Figure 1. Time series panel showing particle growth morphology changes with respect to the electron beam dose rate. At relatively high dose rates cube like formations occur. At medium dose rates an amorphous film is produced throughout the entire viewing area.

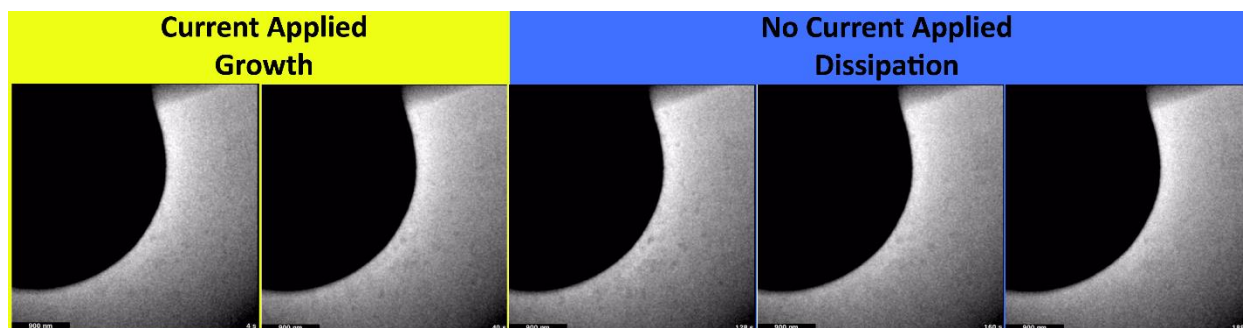


Figure 2. Time series showing the growth and subsequent dissipation of particles. An electrochemical stimulus was applied for 40 seconds and stopped for the remainder of the imaging. Growth is observed until 130 seconds and then dissipation of particles from that point on.

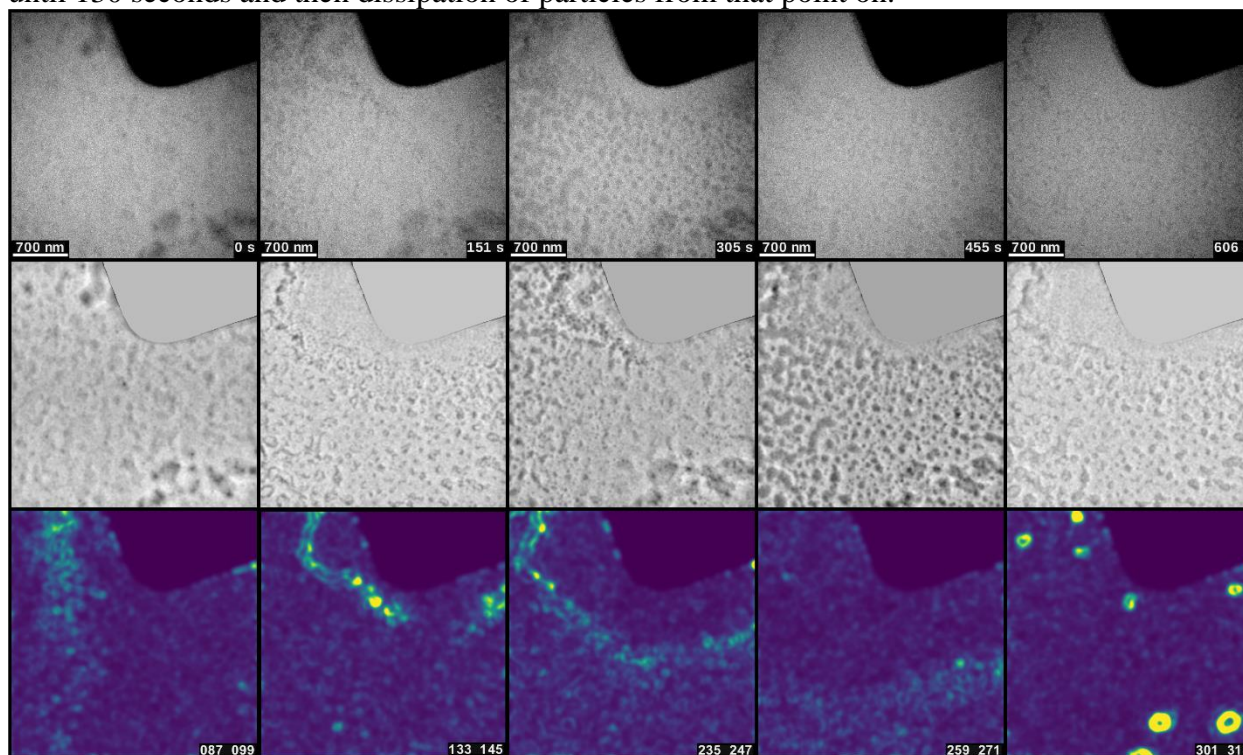


Figure 3. Time series of the CSH system under chronopotentiometric stimulus. **Top Row** shows raw images of the experiment. **Middle Row** shows the modified images. **Bottom Row** is the DISSM analysis of the modified images showing the propagation of a wave associated with increased mass contrast.

- [1] Submission Accepted-In Review; S Selmani et al., *Nature Materials* (2021).
- [2] B Alberts et al. in "Molecular Biology of the Cell. 4th ed." (Garland Science, New York).
- [3] DA Fletcher and PL Geissler, *Annual Review of Physical Chemistry* **60**(1) (2009), p. 469.
- [4] E Mattia and S Otto, *Nature Nanotechnology* **10**(2) (2015), p. 111.
- [5] JL England, *Nature Nanotechnology* **10**(11) (2015), p. 919.
- [6] K Das, L Gabrielli and LJ Prins, *Angewandte Chemie International Edition* (2021).
- [7] RK Grötsch et al., *Journal of the American Chemical Society* **141**(25) (2019), p. 9872.

- [8] J Boekhoven et al., *Science* **349**(6252) (2015), p. 1075.
- [9] M Tena-Solsona et al., *Nature Communications* **8**(1) (2017).
- [10] LS Kariyawasam and CS Hartley, *Journal of the American Chemical Society* **139**(34) (2017), p. 11949.
- [11] A Sorrenti et al., *Nature Communications* **8**(1) (2017), p. 15899.
- [12] S Maiti et al., *Nature Chemistry* **8**(7) (2016), p. 725.
- [13] A Mishra et al., *Nature Communications* **9**(1) (2018).
- [14] E Te Brinke et al., *Nature Nanotechnology* **13**(9) (2018), p. 849.
- [15] J Leira-Iglesias et al., *Nature Nanotechnology* **13**(11) (2018), p. 1021.
- [16] I Colomer, SM Morrow, SP Fletcher, *Nature Communications* **9**(1) (2018).
- [17] WA Ogden and Z Guan, *ChemSystemsChem* (2019).