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In-Situ Low Dose Liquid-Phase Transmission Electron Microscopy of the Electrochemical Polymerization of Poly(3,4-ethylenedioxythiophene) (PEDOT)

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We have been examining the use of low dose liquid phase transmission electron microscopy (LP-TEM) to monitor the electrochemical polymerization of the functionalized polythiophene poly(3,4-ethylene dioxythiophene) (PEDOT). In-situ TEM has been previously used to examine the electrochemical polymerization of a variety of crystalline inorganic metallic, semiconducting, and ceramic materials. However organic conjugated polymers such as PEDOT are much more sensitive to the high voltage electron beam. Furthermore, during solidification they transition through a series of intermediate states from isotropic liquid monomer through viscoelastic oligomers, and finally to solid polymers. The molecules also undergo a dramatic change in their optical properties from clear and translucent to dark and absorbing as the molecular weight increases, and therefore correlative transmitted light optical microscopy has proven to be a particularly powerful method to use in complement with TEM for these studies.

Our work has primarily used a ProtoChips Environmental cell, using microfabricated electrochemical chip with a transparent amorphous carbon substrate as the working electrode. The work has been done primarily at 200 kV in a ThermoScientific Talos F200C STEM located in the University of Delaware Center for Advanced Microscopy and Microanalysis (CAMM). The total doses used in these experiments were around 6-12 e/A^2, which is substantially below the estimated critical doses for PEDOT (~60 e/A^2). The oxidative electropolymerizations were done either galvanostatically (constant current, 150 nA) or potentiostatically (constant voltage, 1.2 V) using a Gamry Reference 600. Optical micrographs were acquired with an Olympus BX60 BF microscope under conditions similar to those used in TEM with a specially designed electrochemical mounting stage from ProtoChips. The EDOT monomer concentration was 0.01M in water, and lithium perchlorate was used as the counter-ion.

We performed several control experiments to insure that the electrochemical deposition we observed in the TEM was associated with the current delivered to the microfabricated chip and not the electron beam. First, we only saw PEDOT deposition on the working electrode itself, never on the surrounding silicon nitride support membrane, Also, we never saw polymer deposition if no current was being delivered to the electrode. We did observe evidence for local bubble formation (presumably solvent degradation) when the beam was focused down to a small spot (less than about 10 mm). We took care to minimize the total dose, following quantitative analyses of beam dose and dose rates that have been discussed by other investigators [1-3].

Our observations have made it possible to directly observe the nucleation, growth, and solidification of the electrochemically-deposited PEDOT oligomer and polymer domains at near-molecular resolution. We have obtained quantitative information about nucleation density as well as the mechanisms and kinetics of PEDOT domain growth and rearrangement. We have been able to define a variety of metrics that distinguish between the characteristics of liquid-like EDOT oligomer and solid-like PEDOT polymer domains. For example, the liquid-like domains are smooth and show evidence for

rearrangements by droplet coalescence and breakup. They are also more clear or translucent in optical microscopy. On the other hand the solid PEDOT domains are locally rough, and remain more sessile after formation [4].

We have also been able to observe the formation of PEDOT nanofibrils due to the addition of various counterions such as poly(acrylic acid) during the electrodeposition process. These nanofibrils had been previously observed post-situ by scanning electron microscopy (SEM) [5]. We have now been able to watch the formation of these highly anisotropic structures on a local scale, providing insight about the local segregation of reactive species that promotes the elongated surface morphology. This information is useful for optimizing the high surface area of these materials as they are utilized for organic biomedical devices and chemical sensors.

We are continuing to explore the use of in-situ TEM for other synthetic variants of PEDOT, as well as the use of different solvents and counter-ions. We are particularly interested in the interaction of solid nanoparticles with the films during deposition, where we expect that the variation in viscoelastic behavior of the conjugated polymer deposit should cause concomitant changes in nanoparticle adhesion [6].

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