

## Chemistry and Structure of Nanomaterials

Successful nanoscale materials fabrication is empowered by a detailed knowledge of the chemistry and structure of surface bound molecules; e.g., the optimization of SAMs, molecular templates, MEMs lubricants, and functionalized nanotubes. We develop, demonstrate, and advance cutting-edge synchrotron metrologies to bring nanoscale materials phenomena to practical applications.

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In potential MEMs lubricants, we have found that the degree of surface ordering in self-assembled monolayers (SAMs) governs the friction properties of the film. *n*-Alkyltrichlorosilanes films with different chain lengths (C<sub>n</sub> films where *n*=5–30) were characterized by near-edge x-ray absorption fine structure (NEXAFS), Fourier transform infrared spectroscopy (FTIR), and atomic force microscopy (AFM). The chain lengths having 12, 16 and 18 carbon atoms were found to be highly oriented with a preferential molecular orientation of the polymeric C-C chains perpendicular to the surface. C5 and C30 SAMs did not exhibit preferential orientation of the alkyl chain and C10 showed partial ordering. Complementary FTIR studies were done to estimate order qualitatively by peak positions of asymmetric CH<sub>2</sub> and the symmetric CH<sub>2</sub> stretches. The molecular order information from FTIR followed similar trends as determined by NEXAFS. The frictional properties of the organic monolayers were determined through the simultaneous measurement of normal (load) and lateral (friction) interfacial forces with AFM. Friction measurements on different chain lengths follow inverse trends with surface order from NEXAFS as shown in Figure 1.

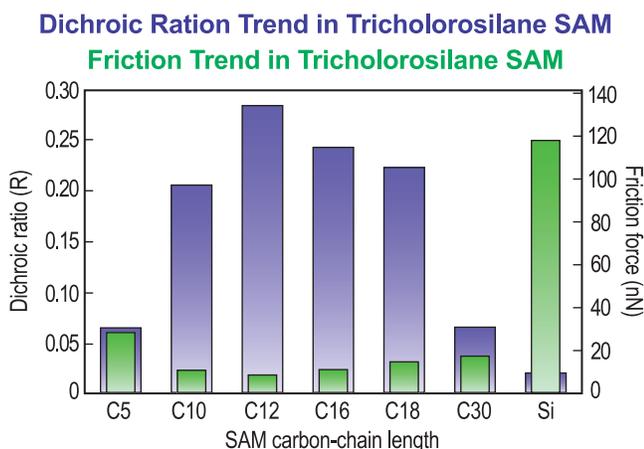


Figure 1: SAM order and friction versus chain length.

The flow-cell developed by NIST for *in situ* ultra-small-angle x-ray scattering (USAXS) studies of solution-mediated nanoscale materials has been applied to the technologically important case of a homogeneously precipitating solution of nanosize ceria (*n*-CeO<sub>2</sub>). *n*-CeO<sub>2</sub> has multiple applications in catalysis, as a solid oxide fuel cell electrolyte material, and in a number of other areas.

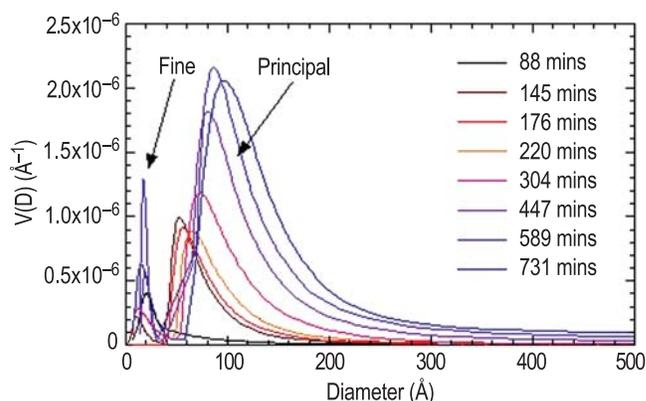


Figure 2: Homogeneous precipitation of *n*-CeO<sub>2</sub>.

Modeling of *in situ* USAXS data taken during reaction at 25 °C indicates a co-precipitation of solid principal particles (see Figure 2) and a population of fine particles with a core-shell morphology. The principal population grows in size and volume fraction, *V*, but the fine secondary features grow only in volume fraction. It has been postulated that the fine features constitute a step in the formation of the principal particle population, a theory currently being tested with additional experiments in conjunction with Columbia University collaborators.

A strong temperature affect is seen: at 35 °C, the volume fraction of principal particles increases with a growth rate roughly twice that at 25 °C. The activation energy for the *n*-CeO<sub>2</sub> precipitation was estimated from USAXS data to be about 46 kJ mol<sup>-1</sup>. Additional studies with the flow-cell focus on dispersion and flow-induced alignment of carbon nanotubes in various solvent/dispersant systems.

### Contributors and Collaborators

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