**New eyes for nanocatalysis:**

**Molecular-scale investigations of nanocatalyst chemistry**

Melissa A. Hines

Dept. of Chemistry and Chemical Biology, Cornell University

The very small size of nanocrystals and the complex milieu of reactants in which they are used has hindered analysis. In this talk, I will review our work in developing “new eyes for nanocatalysts” to help unlock the mysteries of this class of materials.

Over the past few years, researchers around the world have been puzzled by the formation of molecularly ordered structures of unknown origin on the surface of metal oxide photocatalysts exposed to air and solution. Although these structures were initially attributed to a new ordered state of adsorbed H2O, we show that they are due to the self-assembly of atmospheric contaminants present in parts-per-billion concentrations — simple acids! I will discuss why these surfaces selectively adsorb atmospheric organic acids while repelling other small molecules, such as alcohols, present in much higher concentrations. This finding may have implications for TiO2 photocatalysis, as the self-assembled acid monolayer resists desorption under environmental, effectively blocking the transition metal sites typically implicated in photocatalysis. I will also show that this chemistry can also be used to prepare a variety of highly ordered self-assembled monolayers for photoreaction studies.

To address the issue of size, we have developed hydrothermal, heteroepitaxial crystal growth techniques to grow highly aligned, supported nanocrystals that can be studied at the atomic scale using scanning tunneling microscopy (STM) and other surface science techniques. Despite being synthesized in solution, the nanocrystal surfaces are surprisingly clean, which is due to their passivation by a protecting fluorine monolayer. We have used these crystals to gain atomic-scale understanding of catalyst activation, providing a molecular understanding of how a simple aqueous solution increases the reactivity of clean nanocrystals by a factor of five.