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The shape and exposed facets of metallic nanocrystals determine many of their optical and catalytic properties, thus it is important to understand the fundamental mechanisms for controlling their shape. Often, etching steps are used to prepare certain shapes of nanocrystals. To investigate etching mechanisms in noble metal nanocrystals, we use in-situ Graphene Liquid Cell Transmission Electron Microscopy (TEM), which has the necessary spatial and temporal resolution to determine the facets and follow etching trajectories during non-equilibrium etching. Further, we can compare etching trajectories to Monte Carlo simulations of the etching process, which gives valuable mechanistic information about atom removal. By reproducibly controlling the electron beam dose rate on our TEM and the initial etchant concentration in the liquid cell pockets, we have determined that the concentration of etchant dictates the potential and the electron flux determines the etching rate. Changing the potential controls the steady intermediate facets when etching gold nanocubes and rhombic dodecahedrons. Investigating the kinetics of the etching process by varying the beam current shows a first order dependence of the rate of etching on the beam flux hitting our sample. At the end of the etching process when the nanocrystal becomes small, the etching rate slows down as the limiting reactant shifts to the number of edge sites on the nanocrystal. Understanding the mechanism of non-equilibrium etching will inform future synthetic development of nanocrystal shape control.

Refreshments will be served prior to the talk.