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Using Graphene Liquid Cell Electron Microscopy to Elucidate Nanocrystal Etching Mechanisms

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Metallic nanocrystals have applications in a wide array of fields ranging from catalysis to biomedicine, so understanding the mechanisms of nanocrystal shape transformation would allow further tunability of their properties [1]. Kinetically-driven synthesis can lead to unique nanostructures that are not limited by thermodynamics, yet most characterization techniques are unable to follow these shape transformations on the single particle level. We have used graphene liquid cell TEM to controllably study nanocrystal etching trajectories in the nanoparticle's native liquid environment [2].

Previous work by our group has shown the ability to use Graphene Liquid Cell TEM to see intermediate shapes formed during non-equilibrium etching, but this work did not investigate the effects of chemical potential or the electron beam on the etching process [3]. For this work, a solution of aqueous gold nanocrystals, Tris HCl Buffer, and $FeCl_3$, was encapsulated between two sheets of graphene and imaged in the TEM. The combination of $FeCl_3$ and oxidative radiolysis products generated by the electron beam creates a highly non-equilibrium etching environment. Both the {100}-faceted cubes and {110}-faceted rhombic dodecahedra (RDD) etch to intermediate {hk0}-faceted tetrahexahedra (THH) shapes. Using image analysis tools, the facet trajectories of the nanocrystals can be followed at different concentrations of $FeCl_3$ and compared to Monte Carlo simulations where the probability of atom removal depends on the atom's number of nearest neighbor bonds to understand the mechanism of non-equilibrium etching.

Etching gold nanocubes leads to {hk0} THH intermediate shapes with steady h/k values that are dependent on the concentration of $FeCl_3$. Higher initial concentrations of $FeCl_3$ leads to facets with higher h/k values, and this observation of higher driving force leading to higher h/k value facets is corroborated by Monte Carlo simulations. The Monte Carlo simulations show that the edges of the nanocrystal are encompassed by 6-coordinated atoms, and removing one of those atoms reveals 7-coordinated interior atoms. By adjusting the driving force, the probability of removing an edge atom versus interior atom is modulated, leading to different steady facets on the etching nanocrystal.

The etching of gold RDDs in the non-equilibrium regime also leads to {hk0} THH intermediate shapes, but the steady h/k value remains 2.5 regardless of the initial $FeCl_3$ concentration. Monte Carlo simulations show that the steady {hk0} facet does not change with the driving force, and similar to the cubes, the facet is controlled by the probability of removing an edge atom compared to a newly exposed inner atom. When a 6-coordinated edge atom on the RDD is remove, a 6-coordinated interior atom is revealed. Therefore, changing the driving force during etching of RDD does not change the probability of etching edge atoms

versus interior atoms, leading to the same steady facet.

The electron beam also plays a role in the etching process because it generates oxidative species needed for etching. Controllably modulating the electron beam dose rate shows that the etching rate is first order with the number of electrons hitting the sample per unit time. The etching rate of cubes also reveals a crossover point in the limiting reactant at the end of the etching as the cube becomes small. At small sizes, there are less edge sites on the nanocrystal available to etch, causing the edge sites to be the limiting reactant instead of the electron beam generated species.

These graphene liquid cell TEM observations of kinetically-driven nanocrystal shape transformations and the effect of driving force and beam dose rate reveal the mechanisms of hard to study non-equilibrium processes. These insights will inform future synthetic work developing novel nanocrystals with controllable high index facets [4].

References:

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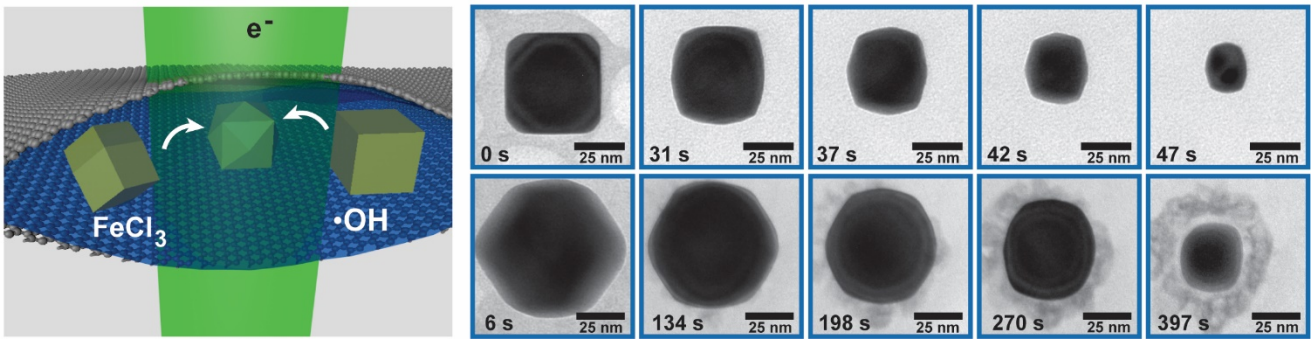

Figure 1. Graphene Liquid Cell TEM using $FeCl_3$ and electron beam generated oxidative species to etch nanocrystals. Both cubes and RDDs transition to intermediate THH shapes with {hk0} facets.

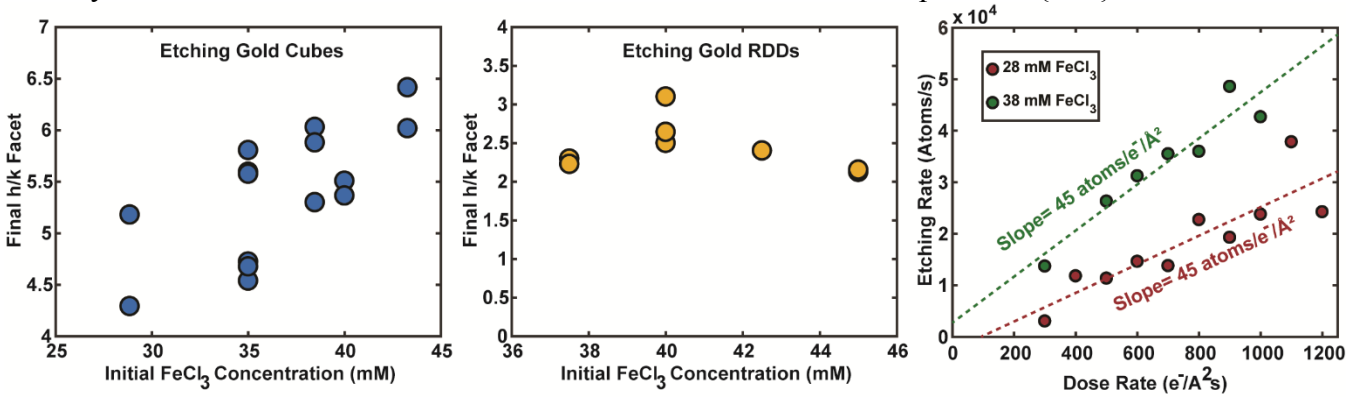

Figure 2. The steady {hk0} facets of the intermediate THH increase with $FeCl_3$ concentration for the cubes but not for the RDDs. The $FeCl_3$ is acting as driving force in the non-equilibrium etching. The etching rate of nanocrystals is also linear with electron beam dose rate.

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