ABSTRACT

Shape, Thermodynamics, Kinetics and Growth Mechanisms of Metal and Bimetallic Nanoparticles

Lingxuan Peng

Metal and bimetallic nanoparticles are of interest and are widely used in various applications because of their unique optical, electronic, and catalytic properties, which differ from those of their bulk counterparts. Better understanding of the thermodynamic and kinetic properties of nanoparticles and their underlying growth mechanisms can serve as a basis for improving reproducibility and rational design of nanoparticle syntheses. The primary objective of this dissertation was to study the structural-related thermodynamic and kinetic properties of nanoparticles via the combination of experimental and theoretical techniques and to further unravel their underlying growth mechanisms.

In this dissertation, the structure and elemental distribution of colloidally-synthesized bimetallic nanoparticles were characterized via scanning/transmission electron microscopy (S/TEM) and energy dispersive X-ray spectroscopy (EDX). In colloidally-synthesized bimetallic Pt/Pd nanoparticles, smooth composition gradients from the particle centers to their surfaces and corner enrichment of Pt were observed experimentally. A growth model was developed to demonstrate that the smooth composition gradients within the particles were the result of the difference in the deposition rate constants of Pd and Pt, causing Pd to deposit faster than Pt. The deposition rate constant ratio between Pd and Pt increased with total Pd and Pt precursor concentration. The corner Pt enrichment was a result of local thermodynamic control at the corners. At the nanoparticle corner, a Lyapunov stable solution could be achieved when the chemical

potential at the corner equals the external chemical potential in the solution. This stable solution leads to size-independent corner rounding in colloidal synthesized nanoparticles.

Strain-induced segregation in bimetallic multiply twinned particles, namely decahedral (Dh) and icosahedral (Ic) particles, was analyzed by an analytic first-order expansion within a continuum model. The results indicated that there was a noticeable segregation of larger atoms to the external surface and the smaller ones to the core, despite a small change in free energy due to segregation. Segregation was found to be more significant in Ic particles compared to Dh particles and at lower temperatures.

The formation of symmetric versus asymmetric particles was also studied to compare their thermodynamic stability. Asymmetric re-entrant decahedral (Dh) particles with mirror planes were synthesized under different conditions. The thermodynamic stability of these particles was analyzed by calculating the total energy of Dh particles at different sizes, and results showed that the nanoparticle size could influence the thermodynamic stable shapes, and the five-fold symmetric Dh shape was no longer the thermodynamic stable structure at bigger sizes.

Beyond electron microscopy, a wide-field dark-field optical microscope was used to measure the diffusion and growth of single plasmonic nanoparticles. The LSPR spectra and diffusion trajectories of particles were obtained simultaneously via an ultra-thin liquid cell. This cell was designed to confine particle movements in 2-D within the depth of field of the objective lens during growth. Being able to monitor changes in both the spectra and diffusion coefficients *in situ* during reaction will open a new avenue for understanding the nanoparticle growth mechanisms.