

MEng Project CHESS-9: Unraveling the Mysterious Mechanisms of Fast Diffusion in Nanoparticles

Matt Ward (CHESS), Richard Robinson (MSE), and Detlef Smilgies (CHESS and CBE)

A grand challenge for nanotechnology is to control and restructure matter at the nanoscale and to understand fundamental growth mechanisms by in-situ analysis of nanoparticle reactions, and phase transformations. A powerful method to atomically restructure the composition and phase of nanoparticles is through chemical transformation reactions, such as the nanoscale Kirkendall effect and the ion exchange reaction (see Fig. 1a). *What is currently unknown in these reactions* is why the ion dynamics behave differently at the nanoscale than in bulk scales. The ion exchange process is orders of magnitude faster in nanomaterials than in bulk materials, but reasons for this rate increase have not been determined. Little information is known about the mechanisms of these reactions. The unique reactivities at the nanoscale are due, in part, to the differences brought about by the decrease in diffusion lengths, interfacial stress, and non-planar reaction interfaces. The proposed work will gain a fundamental understanding of the mechanisms occurring during chemical transformation reactions in nanoparticles. To accomplish this goal we will perform in-situ x-ray absorption spectroscopy (XAS) during the chemical transformations. In situ XAS will permit the study of bond formation kinetics, including amorphous and crystalline contributions, and dynamic information on oxidation states.

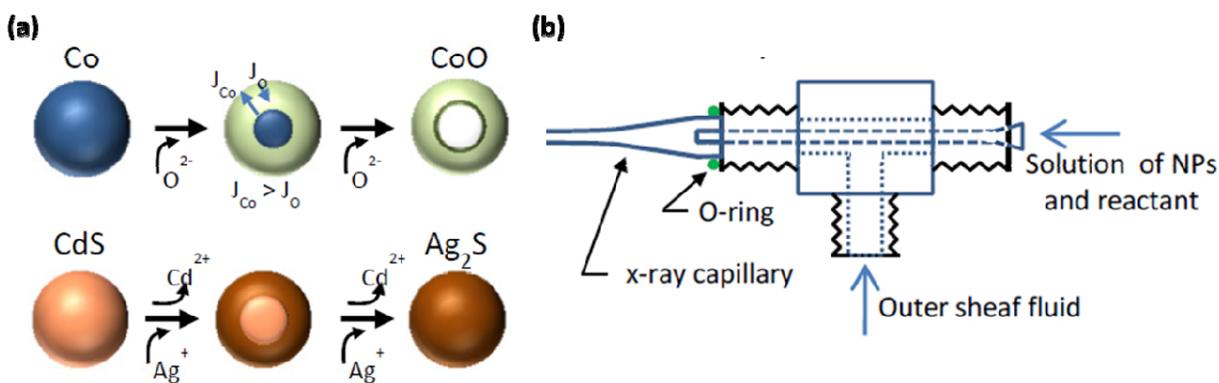


Figure 1. (a) Schematic of two types of chemical transformations on nanoparticles: (top) Redox reaction showing transformation from metallic cobalt nanoparticles into hollow CoO via the nanoscale Kirkendall effect (different diffusion speeds of Co and O). (bottom) Ion exchange conversion of CdS nanoparticles into Ag_2S . (b) Coaxial flow cell for in-situ x-ray absorption spectroscopy of nanoparticle reactions. X-ray capillary (left side) provides spatial-time correlations for time-resolved XAS. Solution of reacting nanoparticles flows coaxially through outer sheaf fluid preventing fouling of the x-ray capillary.

This project will involve the design, fabrication, and testing of flow cells (see Fig. 1b) to study nanoparticle chemical transformation reactions using in-situ x-ray absorption spectroscopy at the Cornell High Energy Synchrotron Source (CHESS). We are looking for a highly motivated student to play a critical role in microfluidic and coaxial flow cell development, fabrication, and testing. The successful candidate will work as part of a multidisciplinary team bringing together substantial expertise in nanoparticle chemical transformation reactions (Prof. Richard Robinson and grad student Andrew Nelson, MSE), x-ray absorption spectroscopy (Matthew Ward, CHESS), flow cell design and fabrication (Richard Gillilan, MacCHESS), and in situ chemical

environments for x-ray probe techniques (Detlef Smilgies, CHESS and Chemical Engineering). Prior experience in microfluidic cell fabrication, fluid mechanics, or nanofabrication techniques is desirable but not required.

Suggested reading

- [1] Yadong Yin, Robert M. Rioux, Can K. Erdonmez, Steven Hughes, Gabor A. Somorjai, A. Paul Alivisatos: "Formation of Hollow Nanocrystals Through the Nanoscale Kirkendall Effect", *Science*, 2004, 304, 711-714.
- [2] Hong Jin Fan, Ulrich Goesele, and Margit Zacharias: "Formation of Nanotubes and Hollow Nanoparticles Based on Kirkendall and Diffusion Processes : A Review", *small* 2007, 3, 1660 – 1671.
- [3] S. Krishnadasan, R. J. C. Brown, A. J. de Mello and John C. de Mello: "Intelligent routes to the controlled synthesis of nanoparticles", *Lab on a Chip*, 2007, 7, 1434–1441.
- [4] A. M. Nightingale, S. H. Krishnadasan, D. Berhanu, X. Niu, C. Drury, R. McIntyre, E. Valsami-Jones and J. C. deMello: "A stable droplet reactor for high temperature nanocrystal synthesis", *Lab on a Chip*, 2011, 11, 1221-1227.