Site-Specific Preparation of Powder for High-Resolution Analytical Electron Microscopy Using a Ga^+ Focused Ion Beam

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Introduction

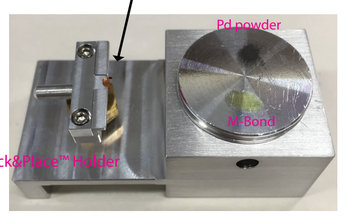
Preparation of powders for high-resolution microscopy presents specific challenges not present in bulk materials. Nanoscale powders (diameters <~100 nm) can be directly deposited on to a TEM grid with drop casting and are usually thin enough for electron transparency in a 200 kV instrument. Microscale powders (diameters ~1 um), on the other hand, must be thinned to electron transparency for high-resolution spatial and chemical analysis. Whereas ultramicrotomy and conventional TEM sample preparation have been able to produce powder particle samples thin enough for high-resolution analysis, this method does not allow for complementary surface analysis on the same powder particle because the particles are encapsulated in epoxy. Any technique that fully encapsulates powder material limits analysis of particle surfaces, and the ability for site specific TEM specimen preparation is reduced using conventional specimen preparation methods. Additionally, both of these methods can take days or weeks to prepare an electron transparent TEM sample. Here, we will demonstrate a technique that enables both surface microscopy and high-resolution cross-sectional analytical microscopy on the same powder particle with diameters larger than 1 um using a Ga+ focused ion beam (FIB).

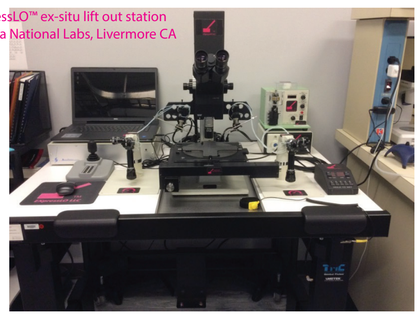
FIB/SEM Sample Preparation

The first step was to get the powder particles onto something that could be mounted into the FIB/SEM. The size of the particles was too large for drop casting, but too small for standard mounting onto an Al stub. Addtionally, due to the combination of mechanical instability and high surface topography of the particles, a standard lift out would have been nearly impossible.

Thus, using an EXpressLO™ ex-situ lift out station, we created the set-up below.

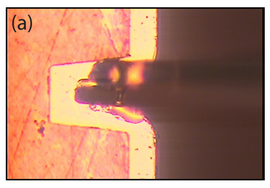
EXpressLO™ grid

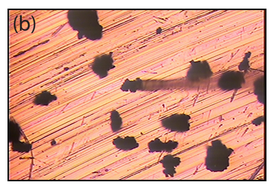




A small amount of powder was sprinkled onto one side of an Al stub. A small amount of M-Bond was placed on the other side of the Al stub. An EXpressLO™ grid was mounted into the horizontally oriented Pick&Place™ holder.

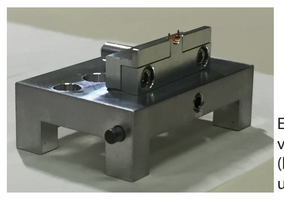
The manipulator was lowered into the M-Bond, picking up a small drop of M-Bond onto the tip. The M-Bond was transferred to an EXpressLO™ grid slot (a). The manipulator was then used to pick up an individual powder particle (b). The particle was transferred to the grid slot (c). This process was repeated several times, filling the grid with multiple particles. The grid was allowed to dry overnight.



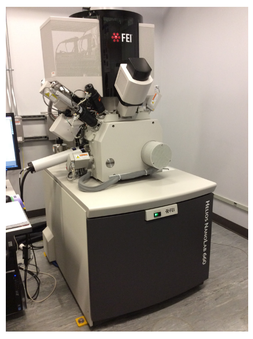


Geometry Matters

The grid was lightly sputter coated with C to reduce charging, and then loaded into an FEI Helios NanoLab 660.



EXpressLO™ Pick&Place™ holder in vertical orientation for FIB milling (holder is sitting in a part of the FEI universal mounting bracket)

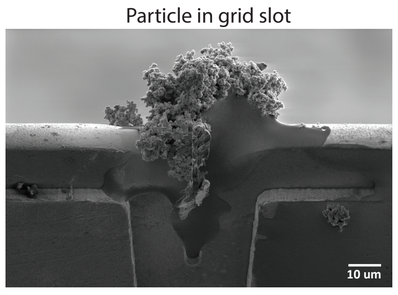


After several iterations of this process, it was determined that placing the particle as far into a grid slot as possible was important for two main reasons:

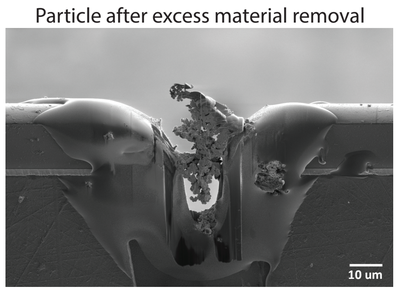
1. The grid slot gives mechanical stability to the particle.
2. The grid slot is area known to work in the TEM.

The first step of FIB milling was to create a slot-shaped particle by shaving away the excess bulk material that protruded out from the top and bottom sides of the grid slot. This ensured that there would be no extra material to block the xray signal from the area of interest from the EDS detector in the TEM. Additionally, this geometry would reduce confusion when attempting to locate the area of interest simultaneously using the FIB/SEM.

Particle in grid slot



Particle after excess material removal

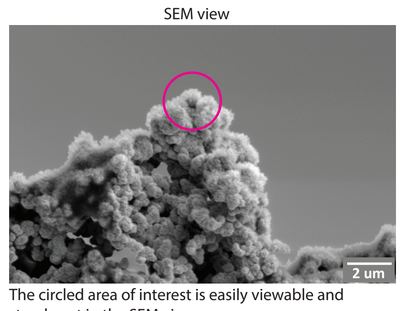


Dual Beam, Dual Perspectives

Using the SEM, an area was identified based on three requirements: 1) surface EDS showed a higher Rd concentration, 2) the area was as close to the top of the particle, 3) the area was sticking out from the main bulk of the particle.

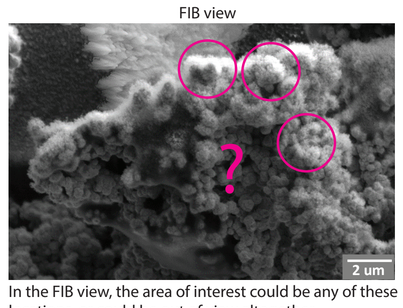
Due to the high surface topography of the particles, the area of interest was challenging to identify in both beams at a stage tilt of 52˚. Below, the same particle is viewed simulatenously at a 52˚ stage tilt.

SEM view



The circled area of interest is easily viewable and stands out in the SEM view.

FIB view

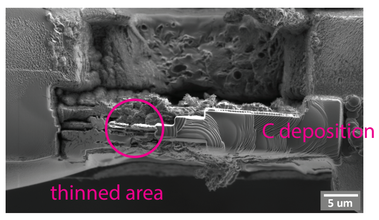


In the FIB view, the area of interest could be any of these locations, or could be out of view altogether.

A small pad of i-beam carbon was deposited onto an area close to but away from the area of interest at a stage tilt of 52˚. The stage was then tilted to 0˚. The i-beam carbon pad was located using the electron beam. The area of interest was identified in relation to the i-beam carbon pad and was then marked using e-beam carbon deposition. Once tilted back to 52˚, the area of interest was then easily identifiable in the ion image.

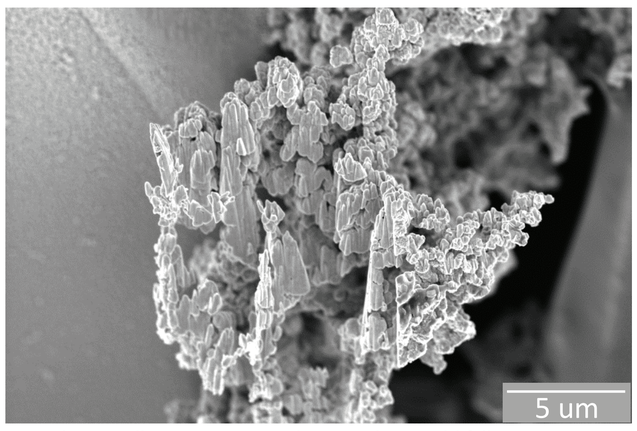
I-beam carbon deposition was placed across the entire width of the top of the particle.

In this top down SEM view, the right side of the image shows the C deposition layer as it appeared before final thinning. The left side shows the area thinned to electron transparency positioned above the foundational particle material and grid slot.

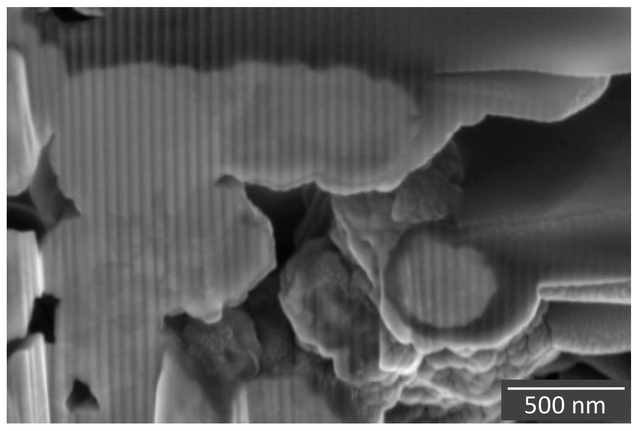


Development of Milling Procedure

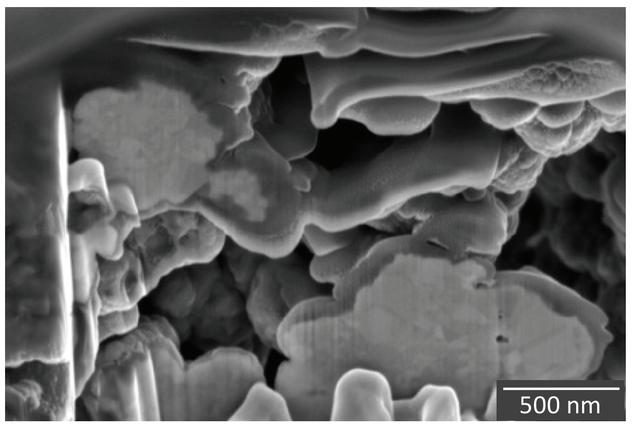
The next challenge was to thin the particles to electron transparency without the particle falling apart. This particular material mills quickly and warps easily using standard milling parameters. Using a milling strategy similar to that which is used for polymers, the particles were milled to electron transparency while still keeping their mechanical structure intact.



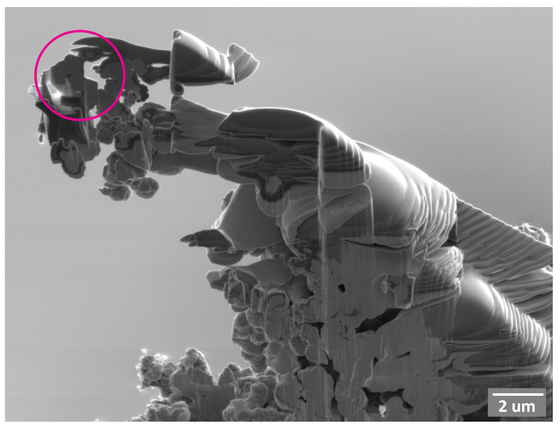
Using basic milling parameters, the particles would fall apart. Here, a regular cross section pattern was used at 30kV and 2.5nA with no adjustment made to the standard FEI Si material file. Overlap 50%, 50%.



Here, the beam current was lowered to 80pA. Additionally, beam overlap was adjusted to -200%, 0%. At this extremely low X overlap setting, you can actually see the the beam path as evidenced by the vertical lines running though the material.



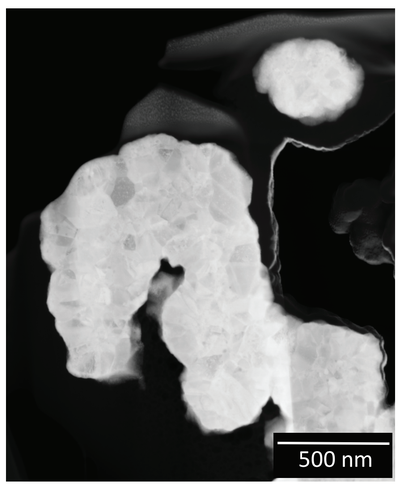
Using the beam path as visual feeback, beam overlap was decreased until a smooth cut was observed. Here, beam overap is -25%, 0%. At this overlap setting, the particles milled evenly and stayed intact.



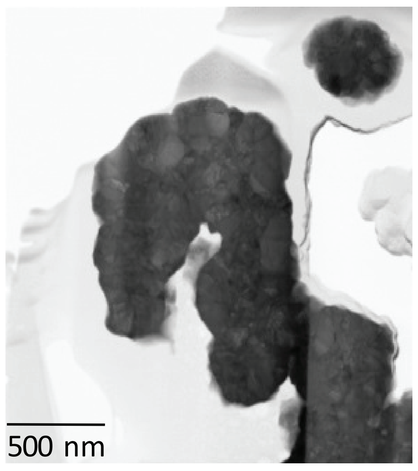
Final thinning was done at 40pA, then 24pA, using the same overlap settings. Electron transparent region circled above.

Successful Atomic Resolution TEM Imaging and Analysis

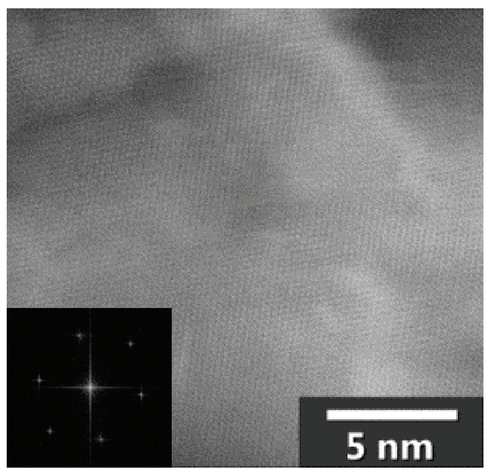
Using these preparation techniques, we were able to obtain atomic resolution images and resolve Rh surface layers between 5 and 20 nm. The samples were characterized both at 30kV in the FIB/SEM and at 200kV in the TEM. In both instruments, the Rh surface layers were resolved and high resolution images were obtained. Addtionally, lattice fringes were imaged in the TEM demonstrating a high quality sample.



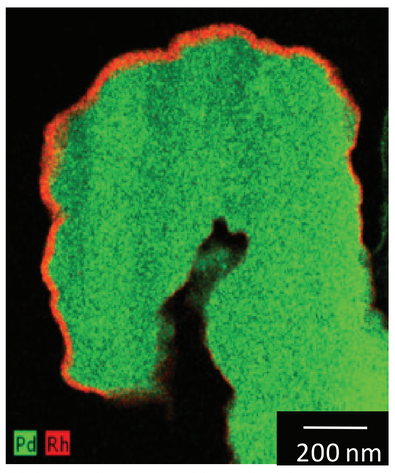
Here, the finished sample is being imaged at 30kV in the FIB/SEM using the STEM detector (HAADF).



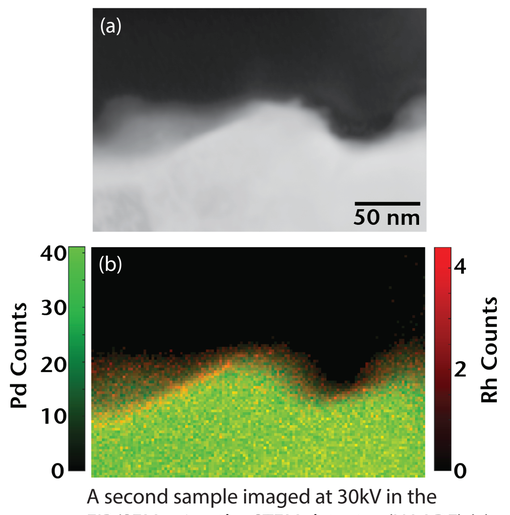
BF STEM image of final thinned (80 nm thick), electron transparent Rh-alloy particle taken in an FEI Titan TEM at 200kV.



Atomic resolution HAADF STEM image of the same particle and corresponding FFT (inset).



EDS reveals a 20 nm Rh surface layer.



A second sample imaged at 30kV in the FIB/SEM using the STEM detector (HAADF) (a). EDS reveals a 5 nm Rh surface layer (b).

Conclusion

Microscale powder particles of various shapes and sizes can be thinned precisely and efficiently using a Ga^+ FIB. Creative mounting techniques combined with specialized milling conditions allow for samples to be thinned to ~80 nm or less. This repeatable technique produces ultra-thin, site-specific samples that provide both high-resolution EDS analysis and atomic resolution imaging in just a matter of hours.

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