SAND2011-3060C

Structural and Compositional Stability of Nanoporous Pd/Rh Alloy Powders

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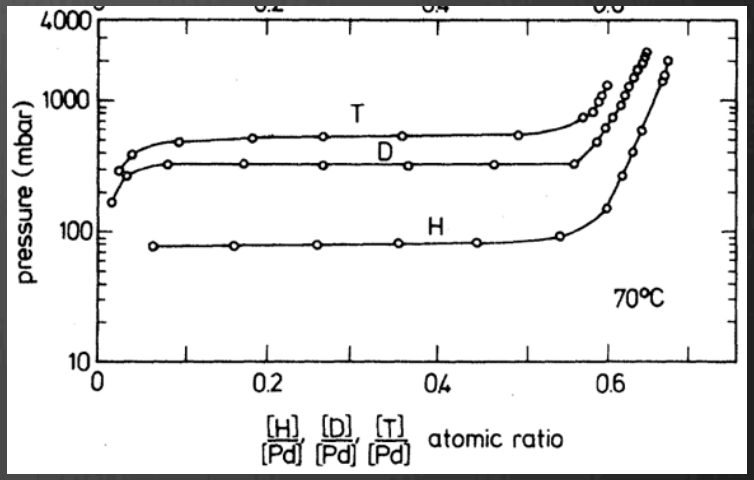
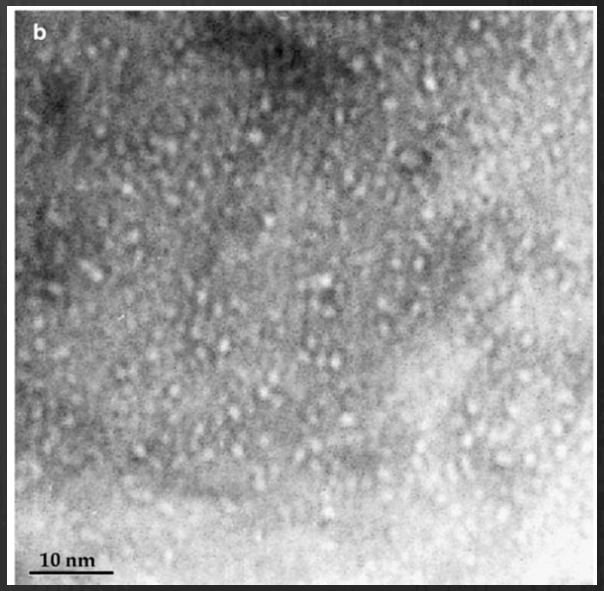
Materials With Large Surface Area

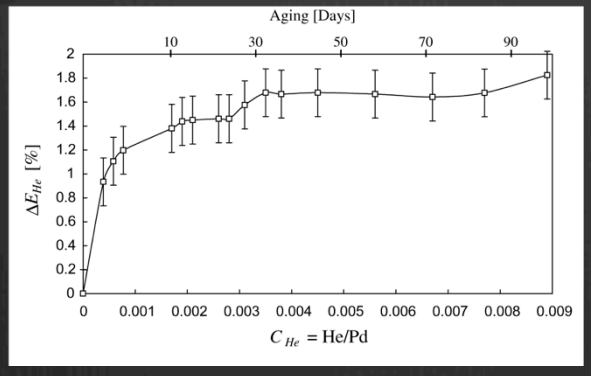
- FF: Surface and nanomaterials for catalysis
- Nanoporous materials for hydrogen isotope storage
  - High surface area can improve surface-limited reaction rates
  - Provides an escape path for helium decay product
    - He bubbles can cause stiffening of bulk Pd



Lässer, *PRB*, **26(6)**, 1982



Fabre et al., *J Nuc Mat*, **342**, 2005



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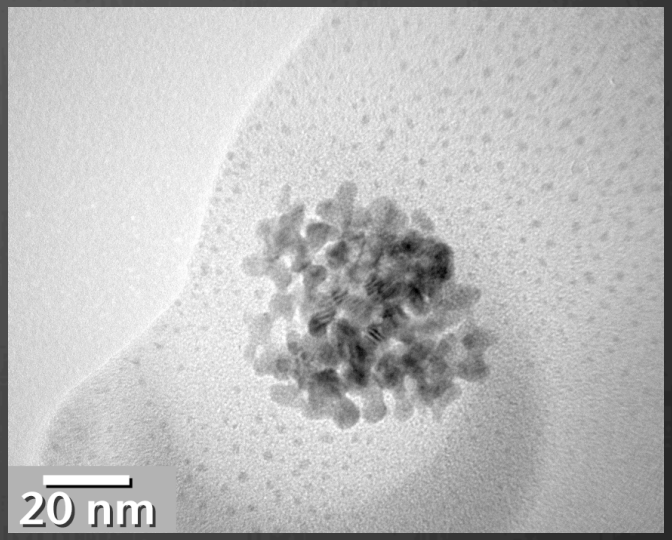
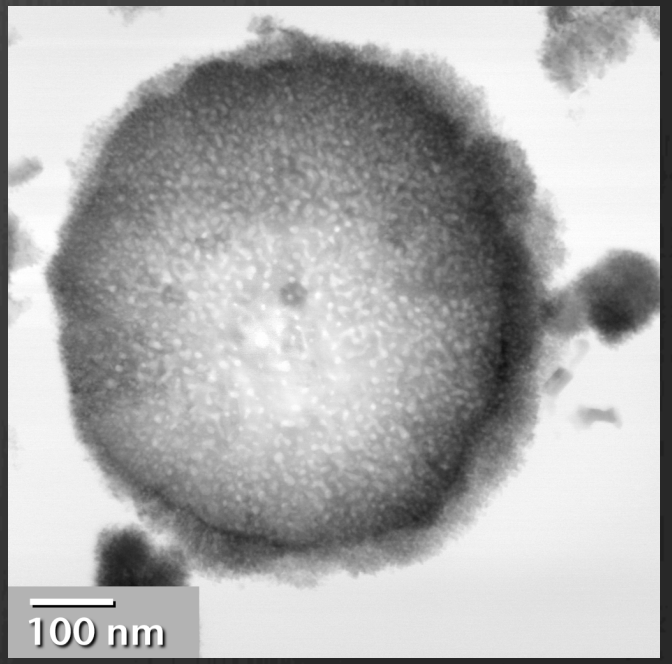
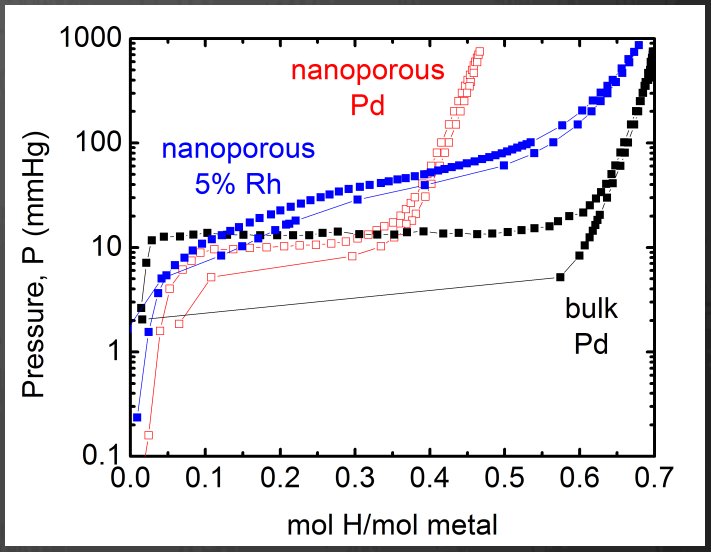
- FF: Surface and nanomaterials for catalysis
- Nanoporous materials for hydrogen isotope storage
  - High surface area can improve surface-limited reaction rates
  - Provides an escape path for helium decay product
    - He bubbles can cause stiffening of bulk Pd
- What controls pore structure?
  - Uniformity during formation
  - Collapse at elevated temperature

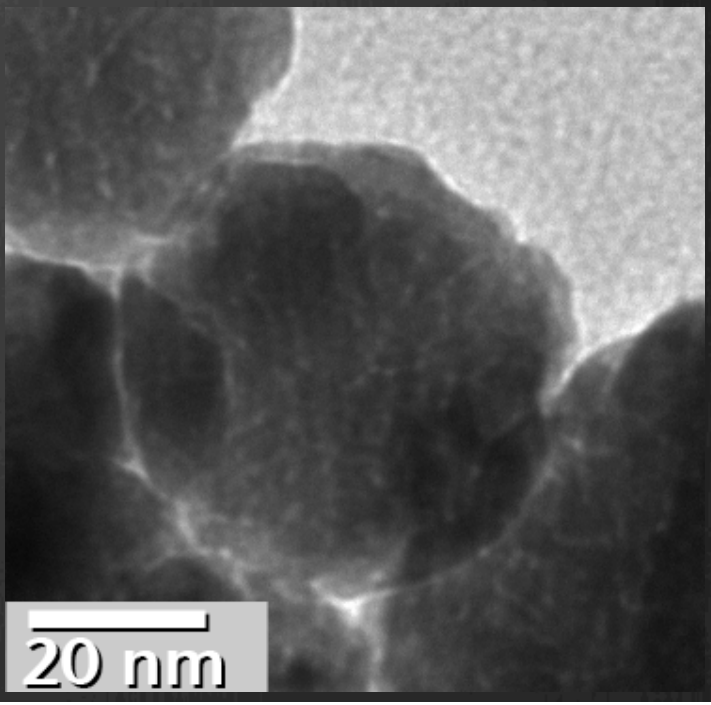




Nanoporous Pd/Rh alloys for H Storage

- Nanoporous Pd shows reduced capacity
- Bulk Pd/Rh alloys show promise for H storage
  - No reduced capacity





Room Temperature

Nanoporous Pd/Rh alloys for H Storage

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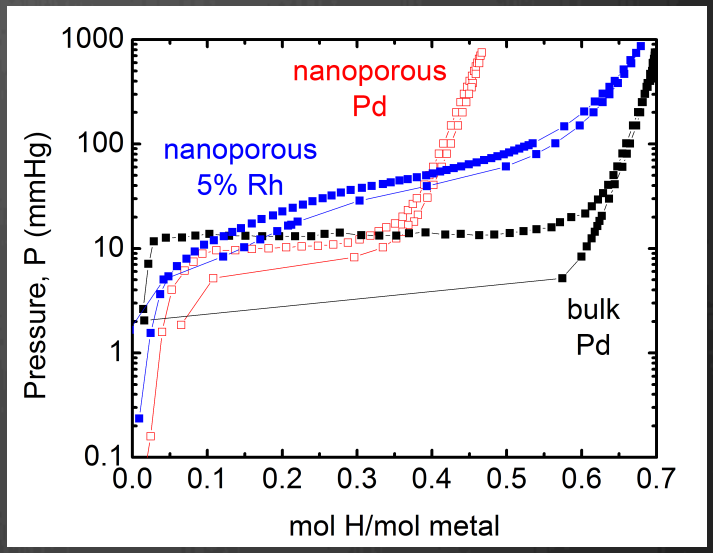
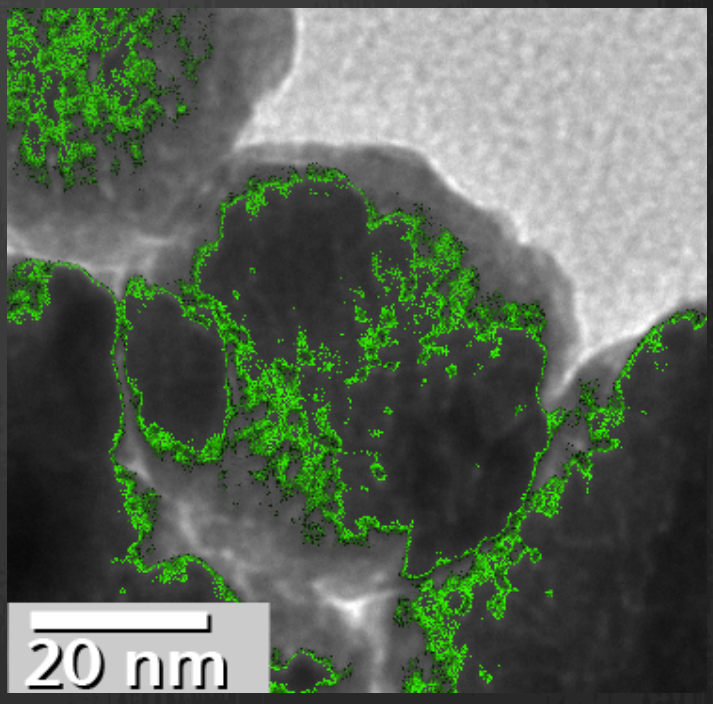
- Nanoporous Pd has poor elevated temperature stability





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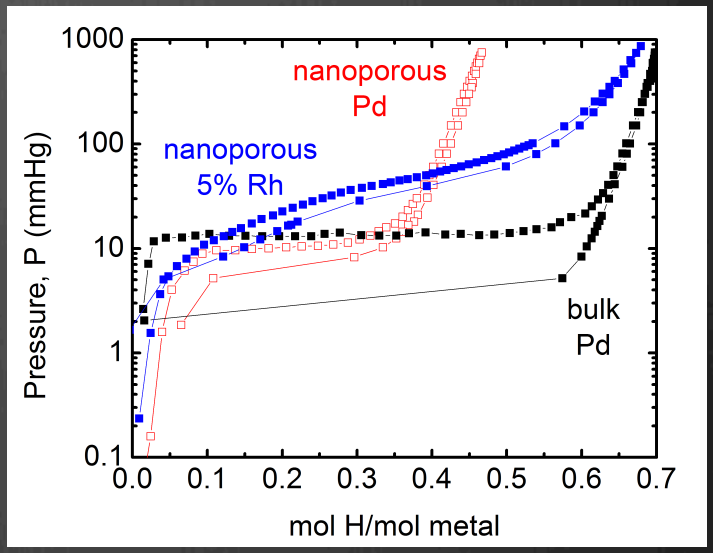

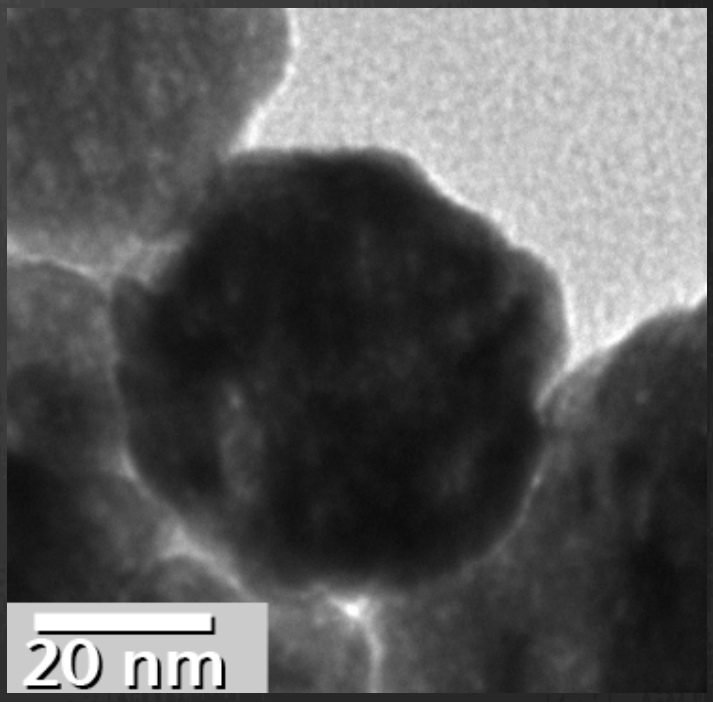

200 ° C
12 min

Nanoporous Pd/Rh alloys for H Storage

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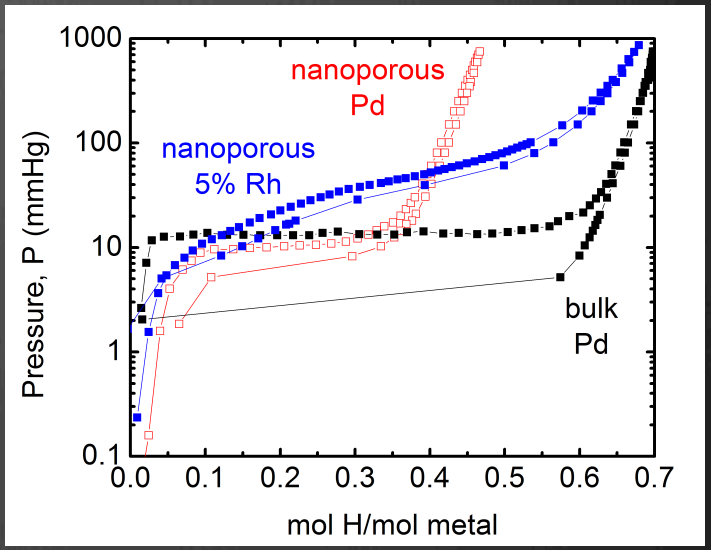
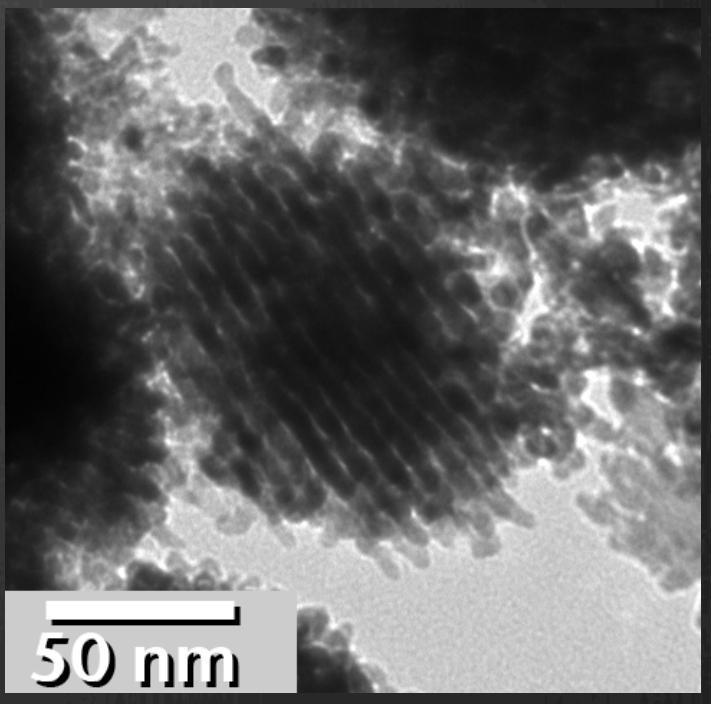
- Nanoporous Pd has poor elevated temperature stability
  - $T_{melting}$ Pd=1555°C
  - $T_{melting}$ Rh=1963°C
    - 200°C is $0.26T_m$ Pd and $0.21T_m$Rh
  - Is the pore structure uniform?
  - Is the Rh uniformly distributed?

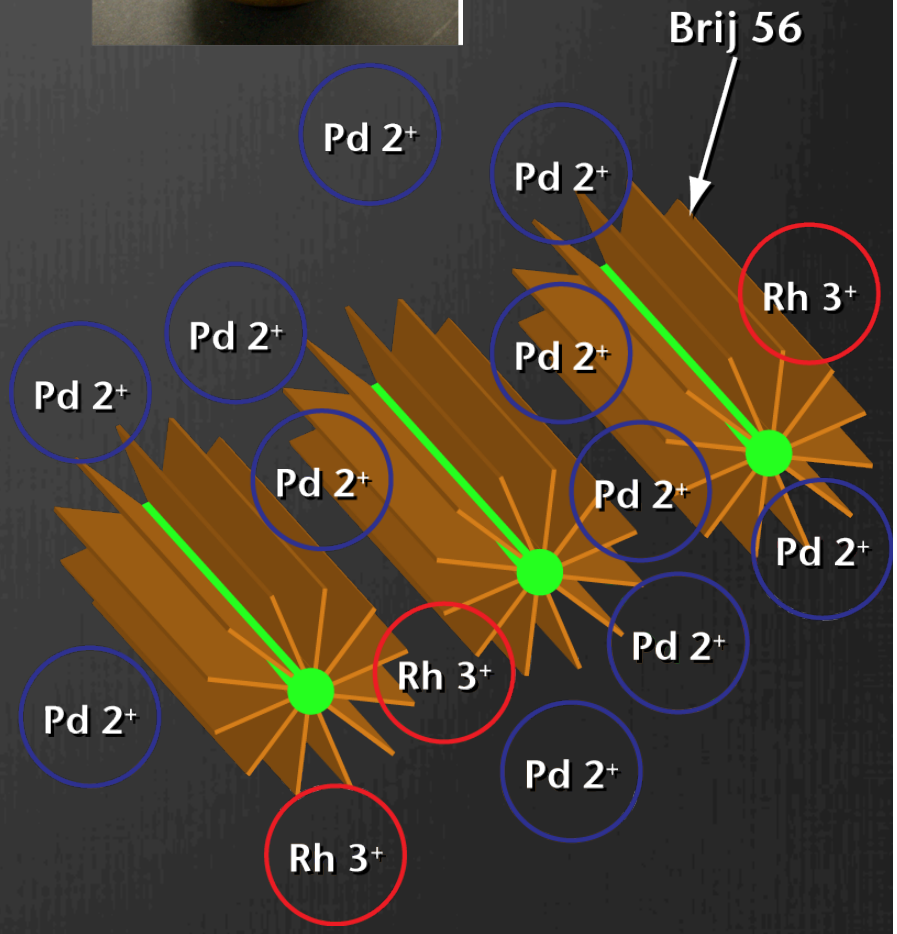




200 ° C
30 min

Surfactant Template Fabrication

- Long organic molecule looks like a pipe cleaner Brij 56
  - Hydrophobic center
  - Solution of metal salts



Robinson, D. et al., *IJHE*, **35** (2010).

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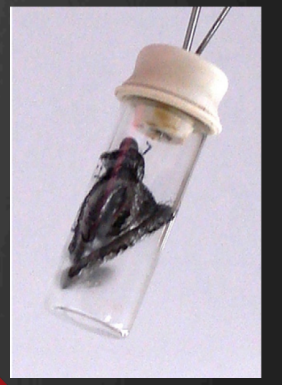
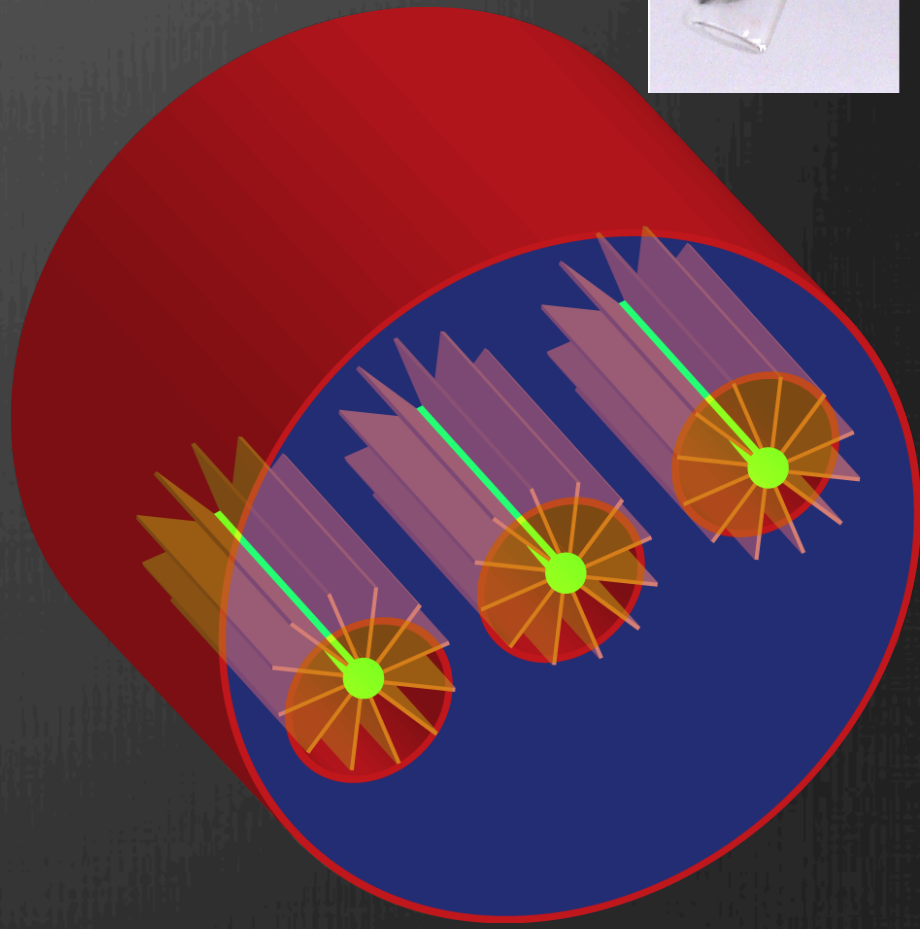
- Reduce the metal salts in flowing gas
  - $(NH_4)_2PdCl_4 + H_2 \rightarrow Pd + NH_4Cl + 2HCl$
  - $2Na_3RhCl_6 + 3H_2 \rightarrow 2Rh + 6NaCl + 6HCl$





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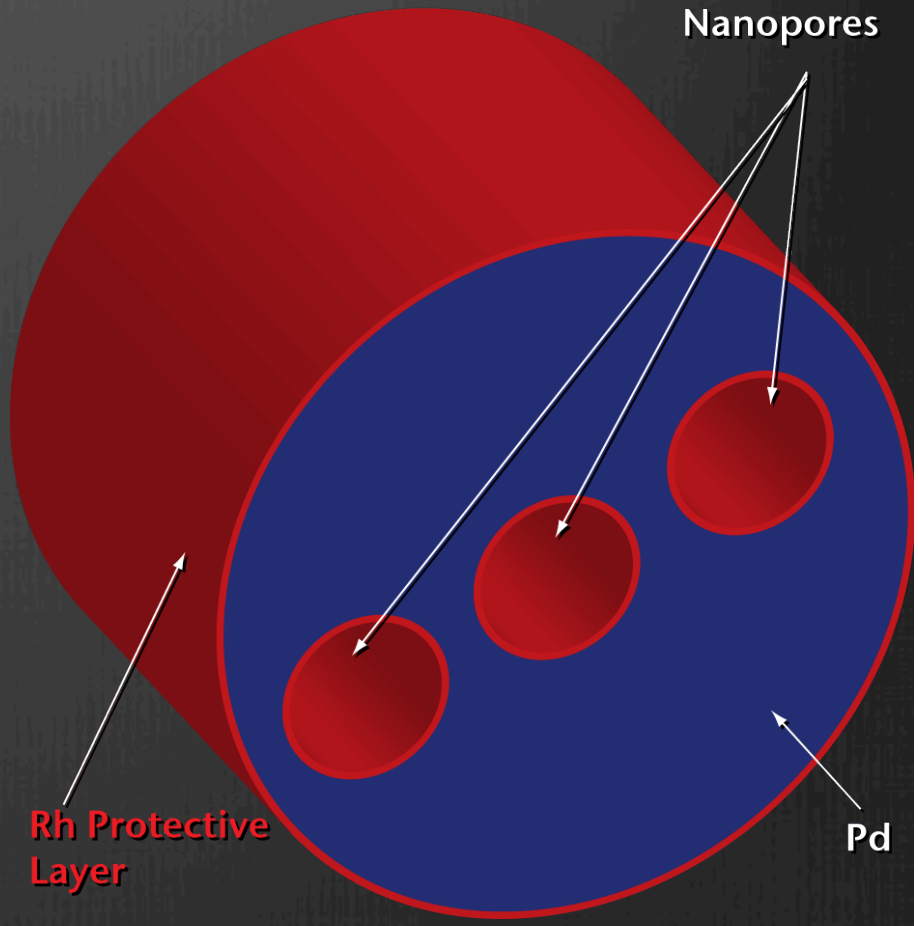
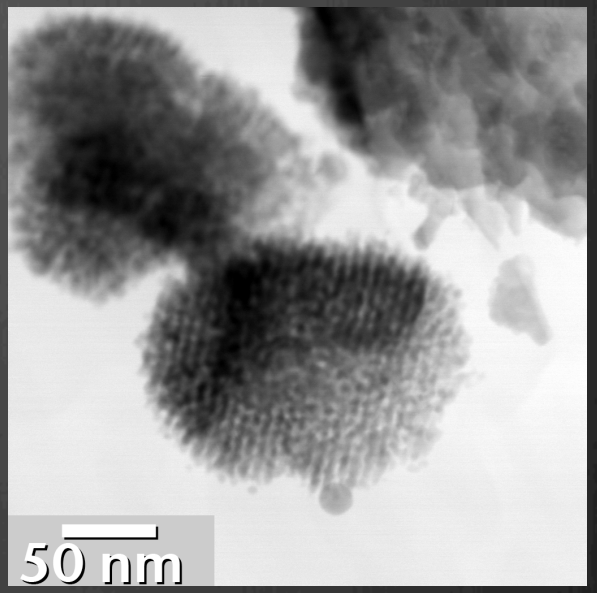
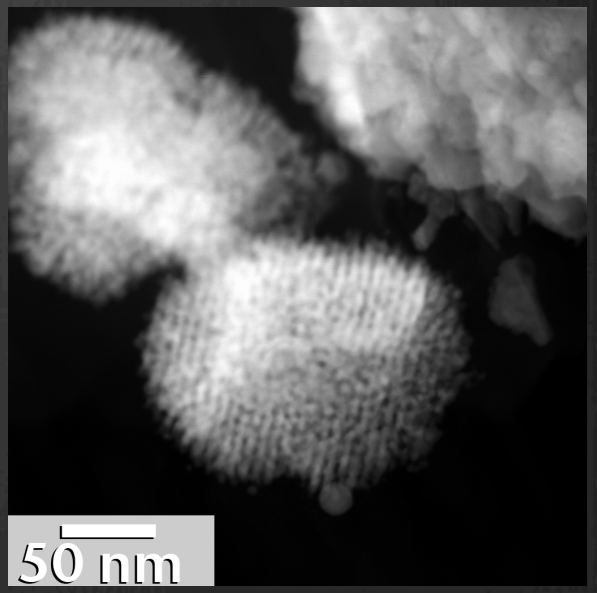
- Rinse off organic residue
- Nanoporous material
- Did it work?



Non-uniformity in 5 at. % Rh-Pd Pore Structure

- Small particles (<100 nm) appear to have regular pore structure





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- Small particles (<100 nm) appear to have regular pore structure
- Larger particles (>100 nm) have irregular pore structure
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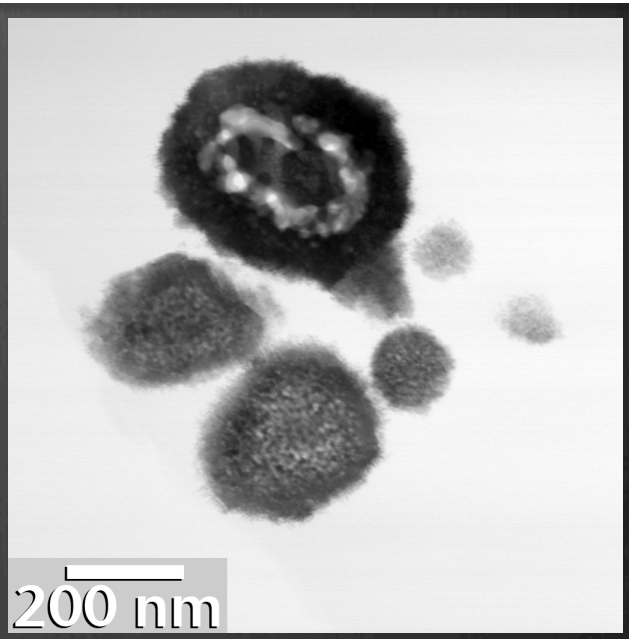
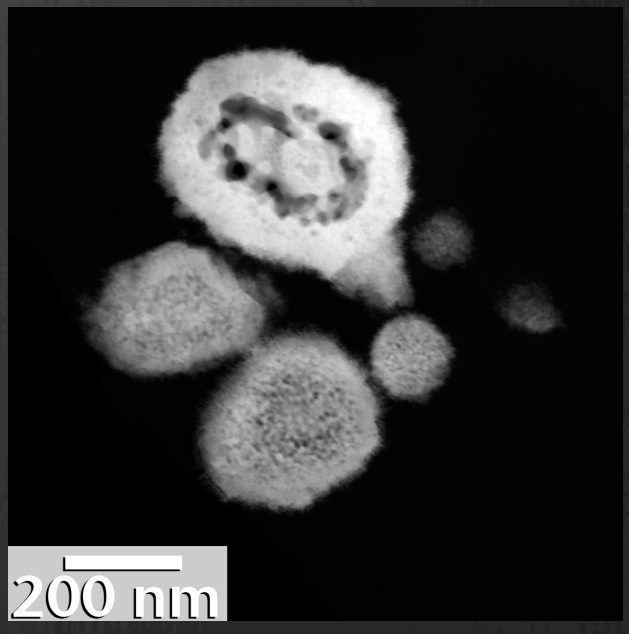
    - Dimple and ion milled
  - Larger pores in core





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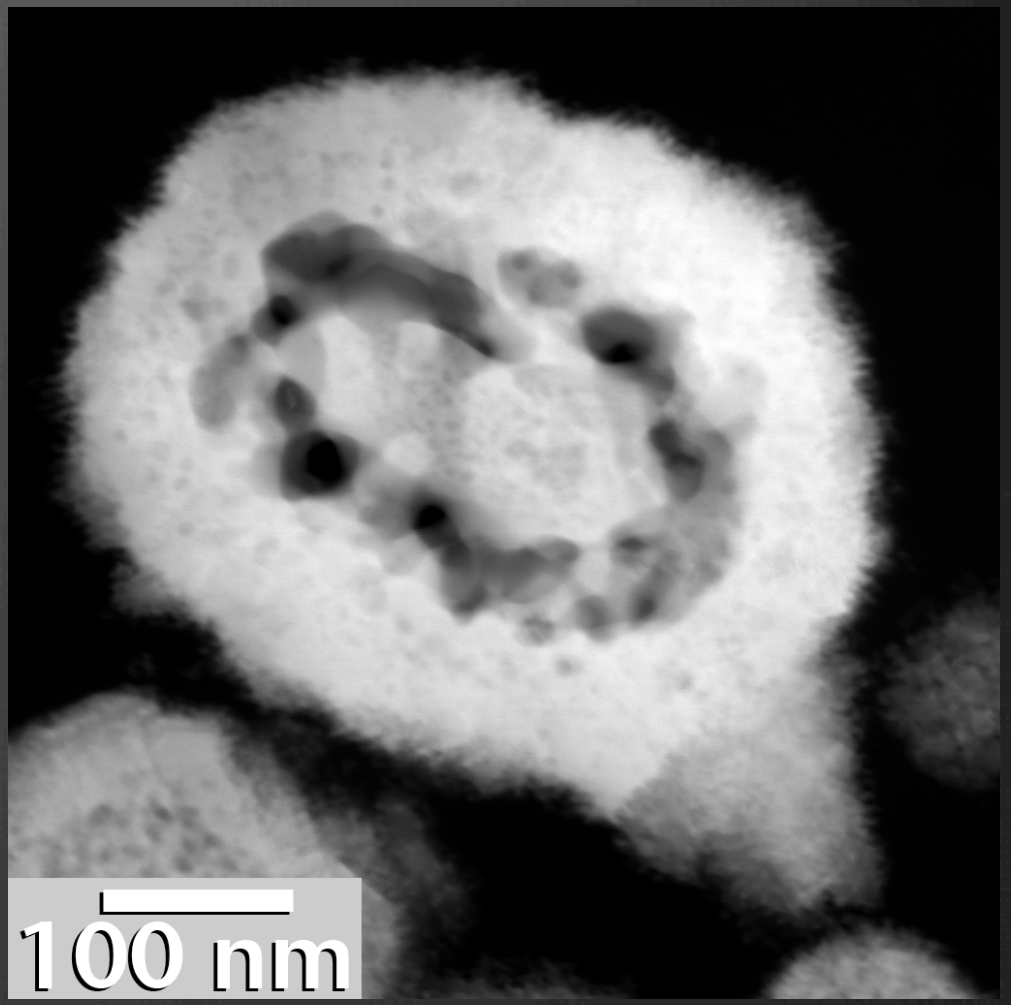
- Compositional uniformity?



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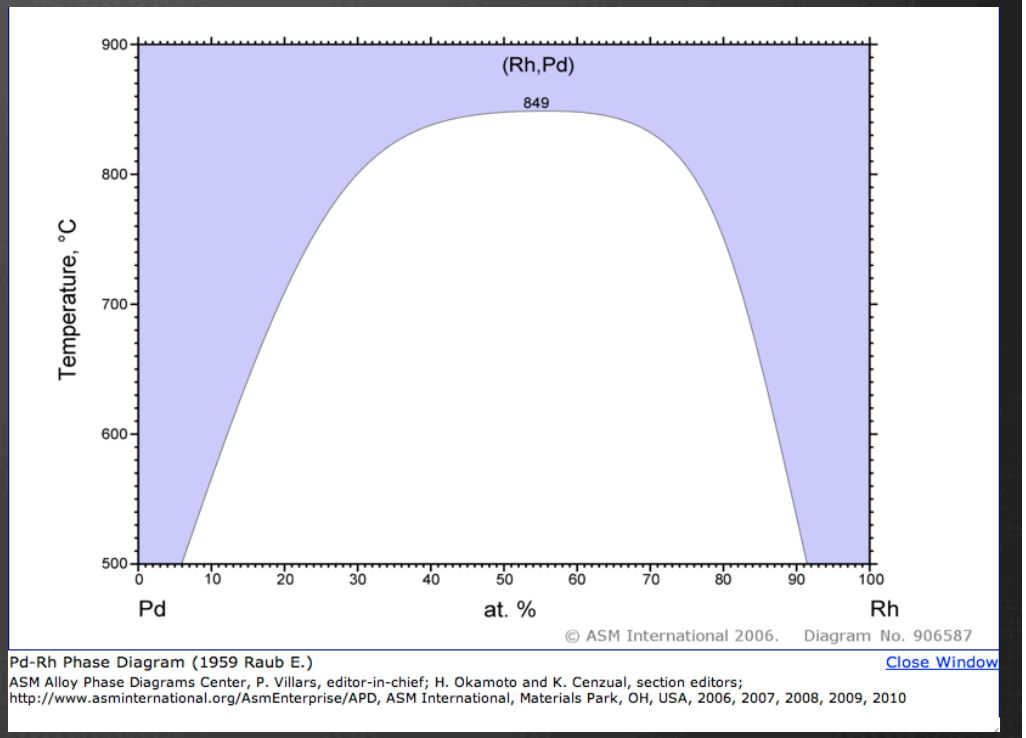
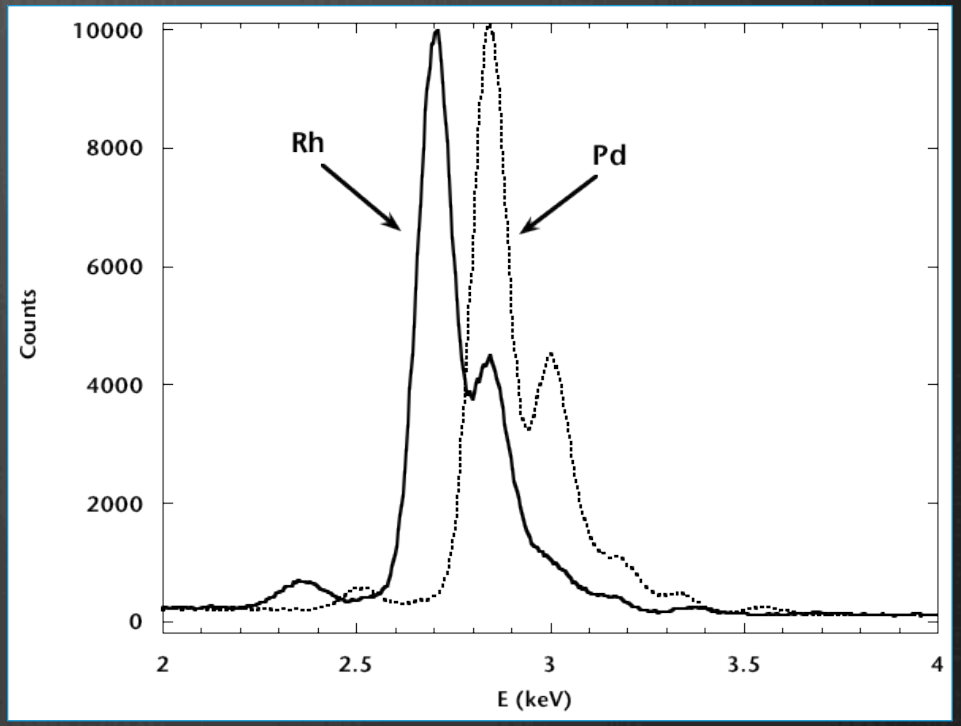
  - Analytical microscopy



Raub, E. *Z. Metallk.* **50** 1959

STEM-EDS Quantification

- EDS spectrum imaging
  - Spectrum at every pixel
  - Overlap of PdL and RhL



STEM-EDS Quantification

- EDS spectrum imaging
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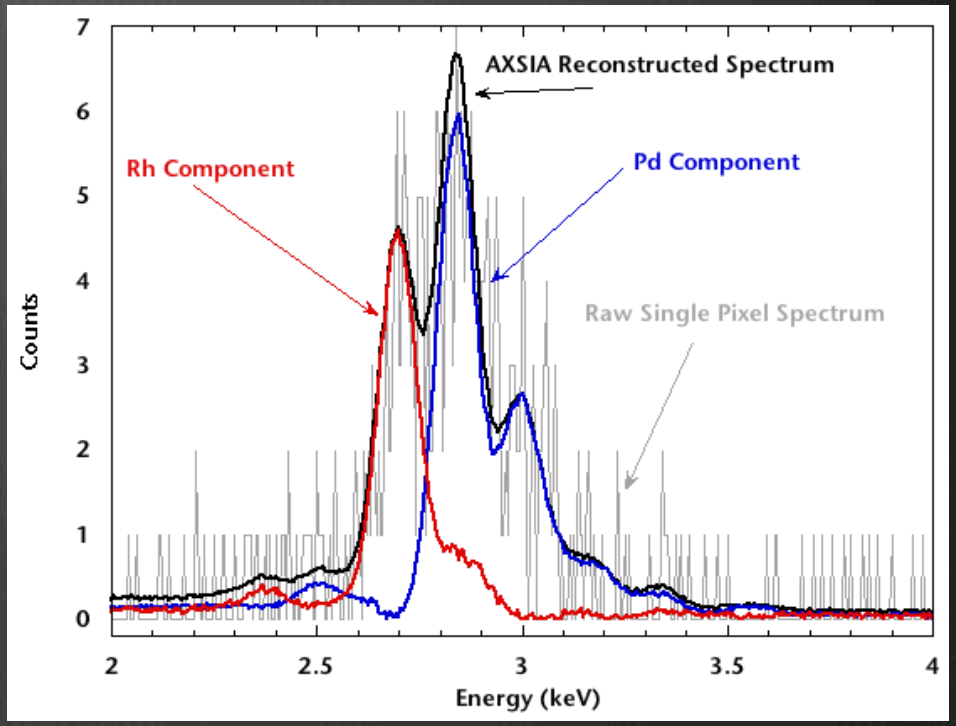
- Multivariate Statistical Analysis
  - Decomposition of data matrix
    - $D=C*S^T$
      - C is matrix of spectral weight at each pixel
      - S is a "pure" component spectrum
    - Weighted for Poisson Statistics
    - Rotated for spectral simplicity
  - Kotula PG, et al. Microsc Miroanal 2003;9:1.
  - Keenan MR. Surf Interface Anal 2009;41:79.
  - Reconstruct the denoised data matrix D



Core/Shell Compositional Distribution

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  - Spectrum at every pixel
  - Overlap of PdL and RhL
- Multivariate Statistical Analysis
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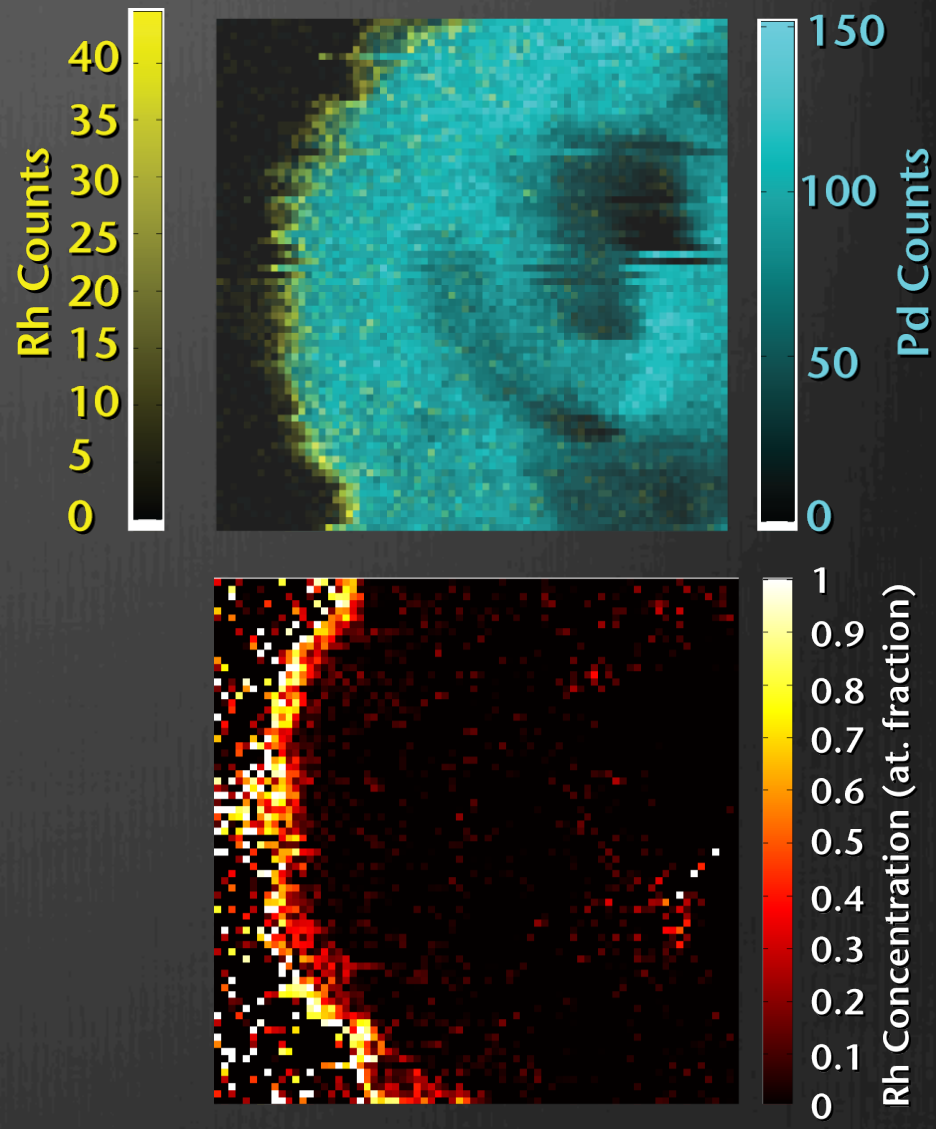
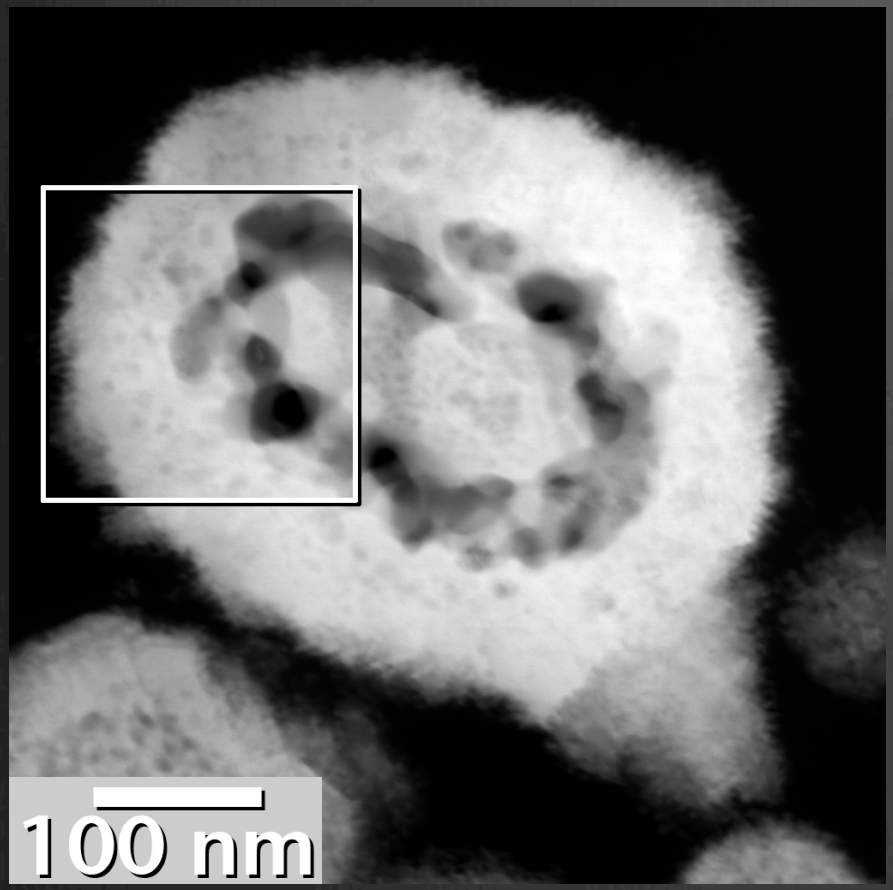
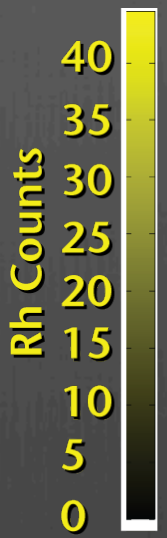
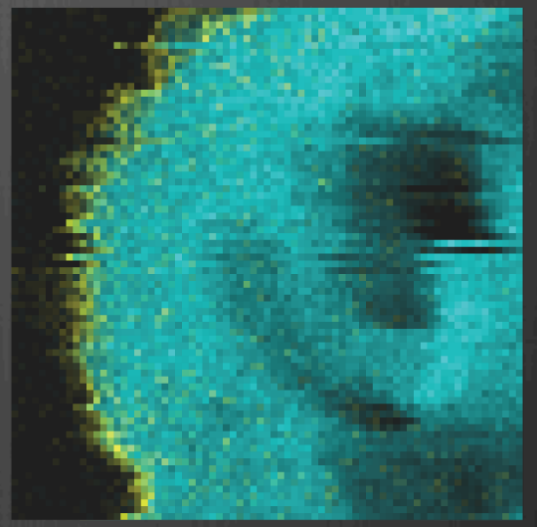
- Multiple Least Squares Fit and Cliff-Lorimer Ratio
  - Cliff G, Lorimer GW. *J Microsc-Oxford* 1975;103:203.

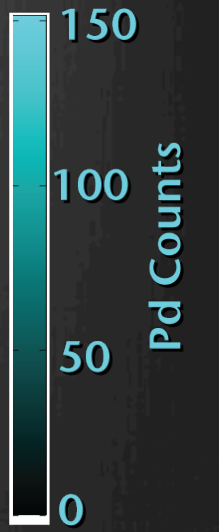


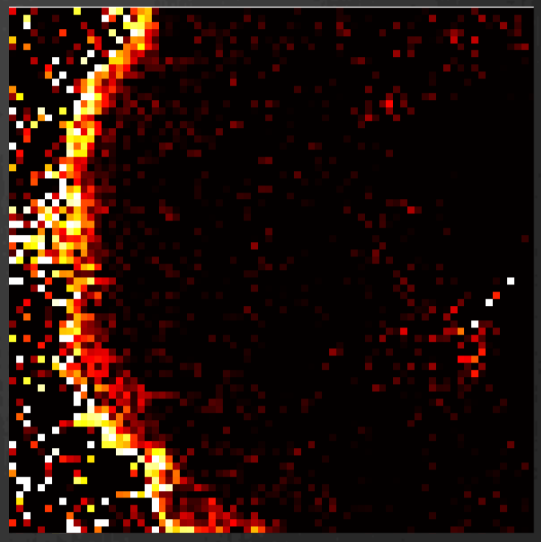
Core/Shell Compositional Distribution





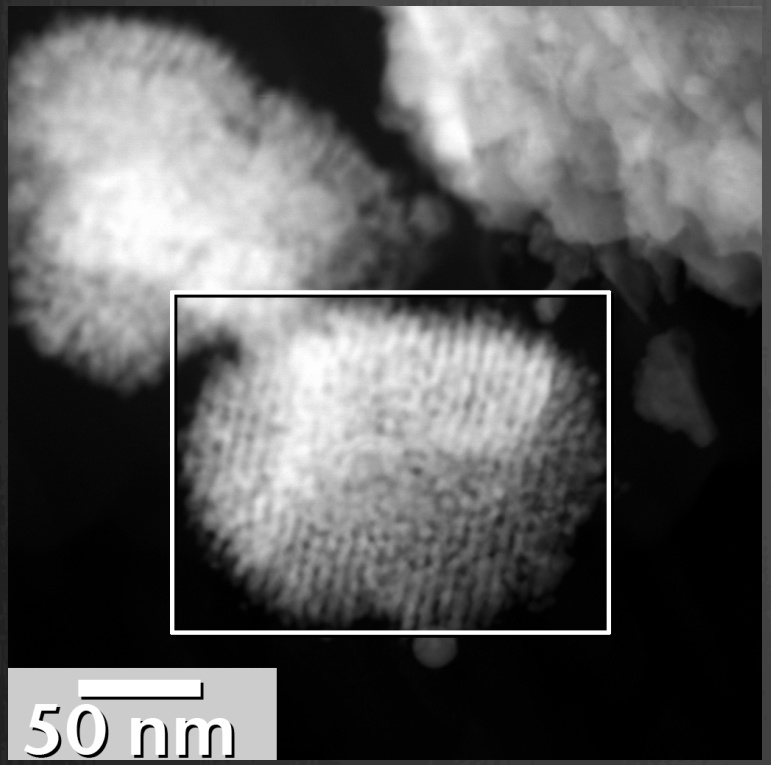


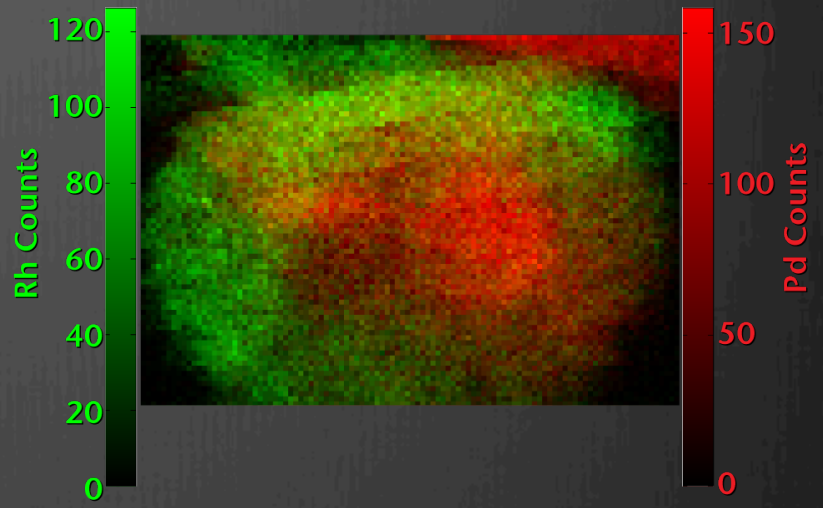


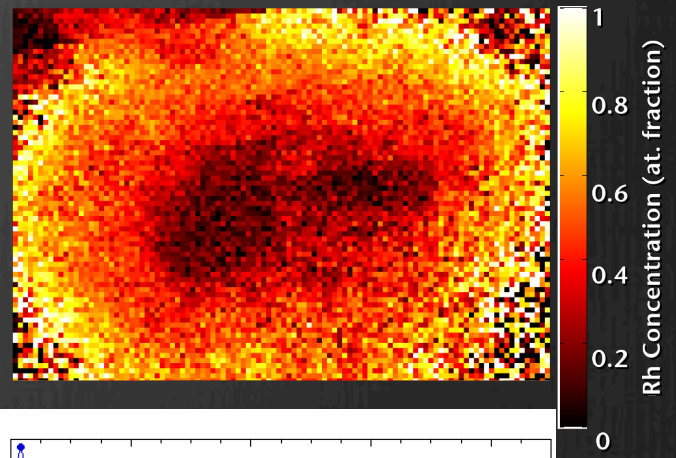


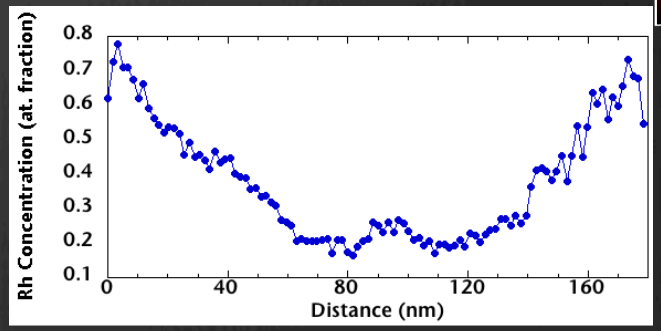
What about smaller particles?

Core/Shell Compositional Distribution



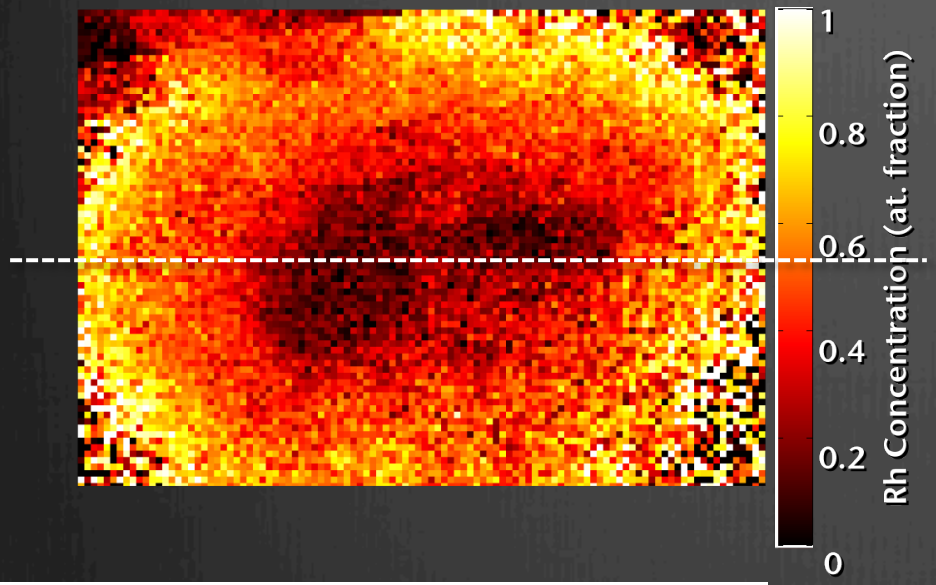


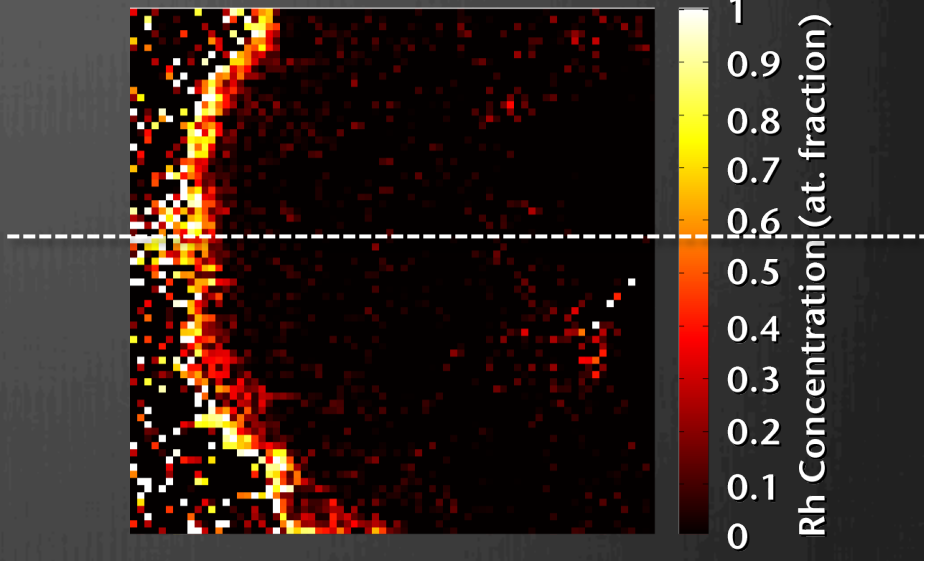


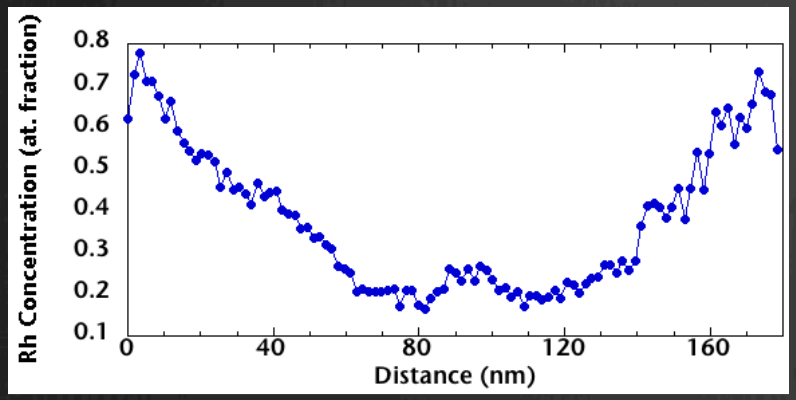


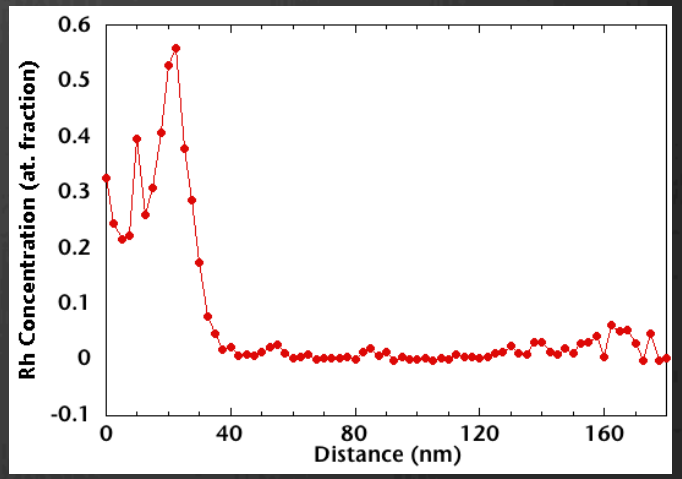
- Core/Shell
- Evidence of Coalescence

Smaller Particles: More Gradual Rh









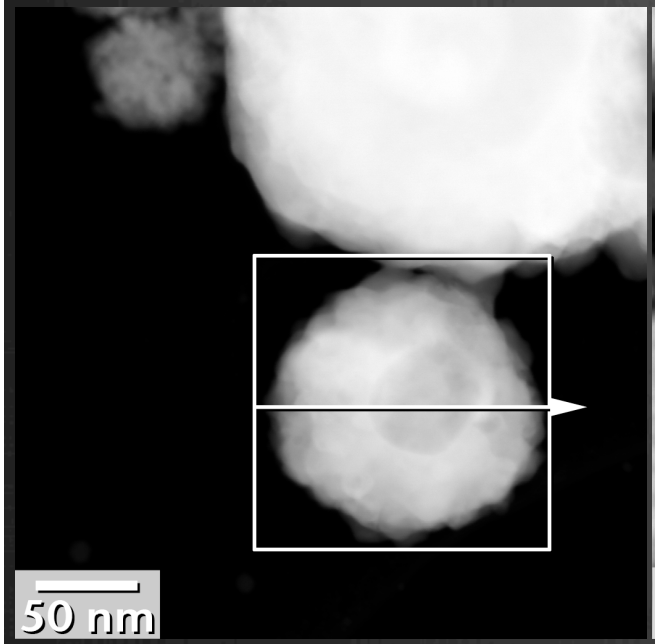
More Gradual Rh distribution ➔ More Uniform Pore Size Distribution

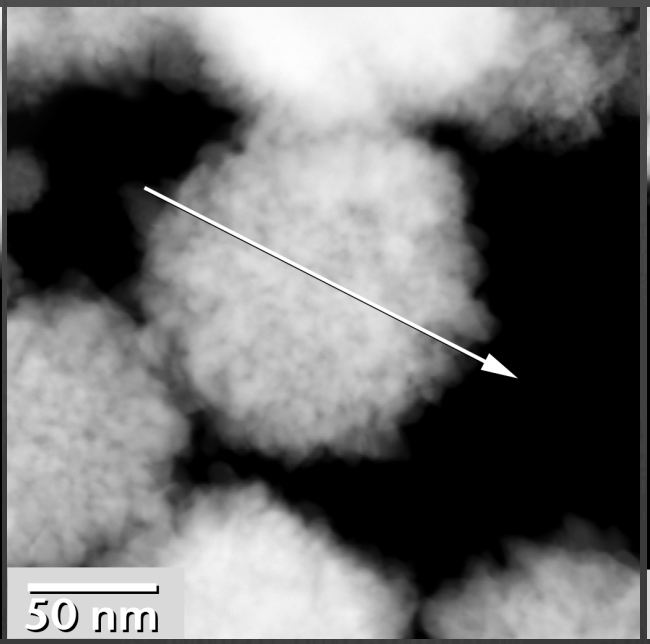
Higher Rh Content: More Ordered Pores

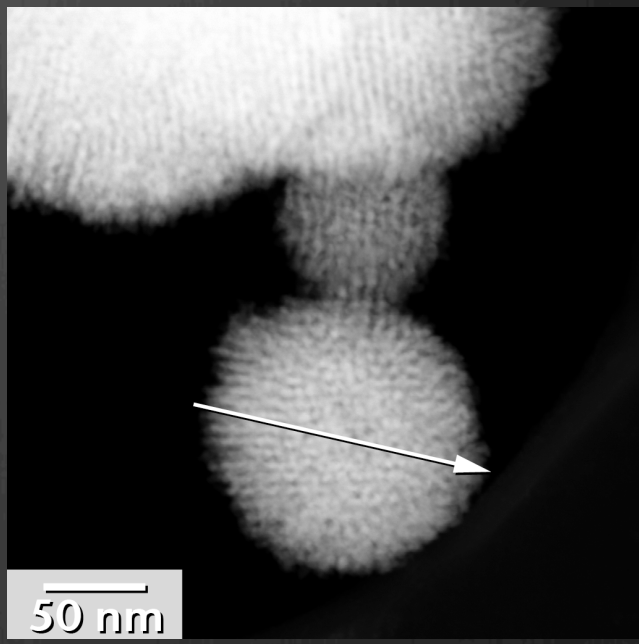
5 at. % Rh-Pd

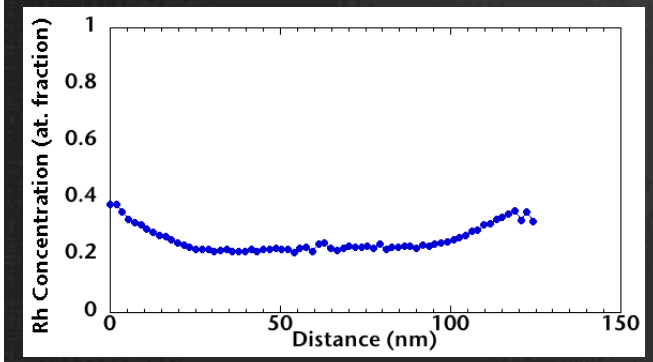
10 at. % Rh-Pd

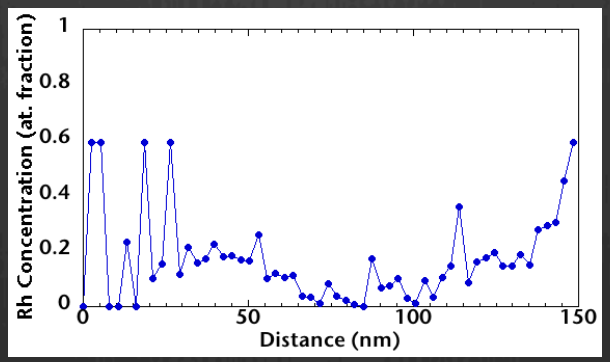
50 at. % Rh-Pd

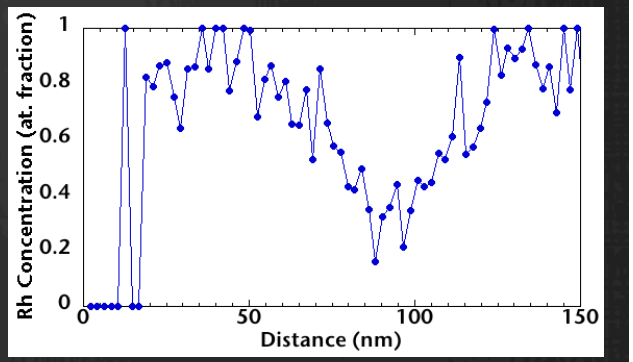






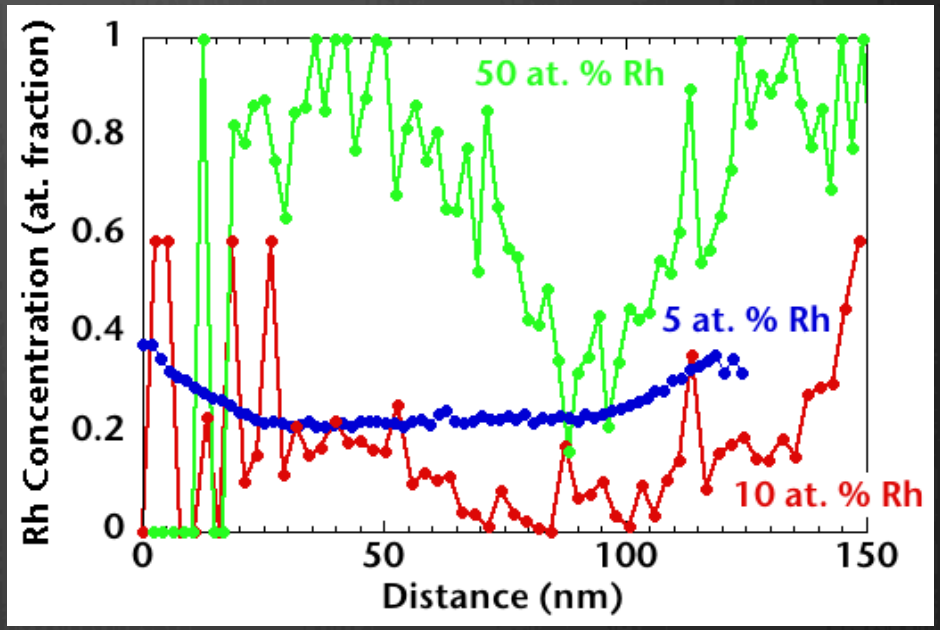






Diffusion-Limited vs. Reaction-Limited Processes

- Averages all seem high (particles ~100 nm)



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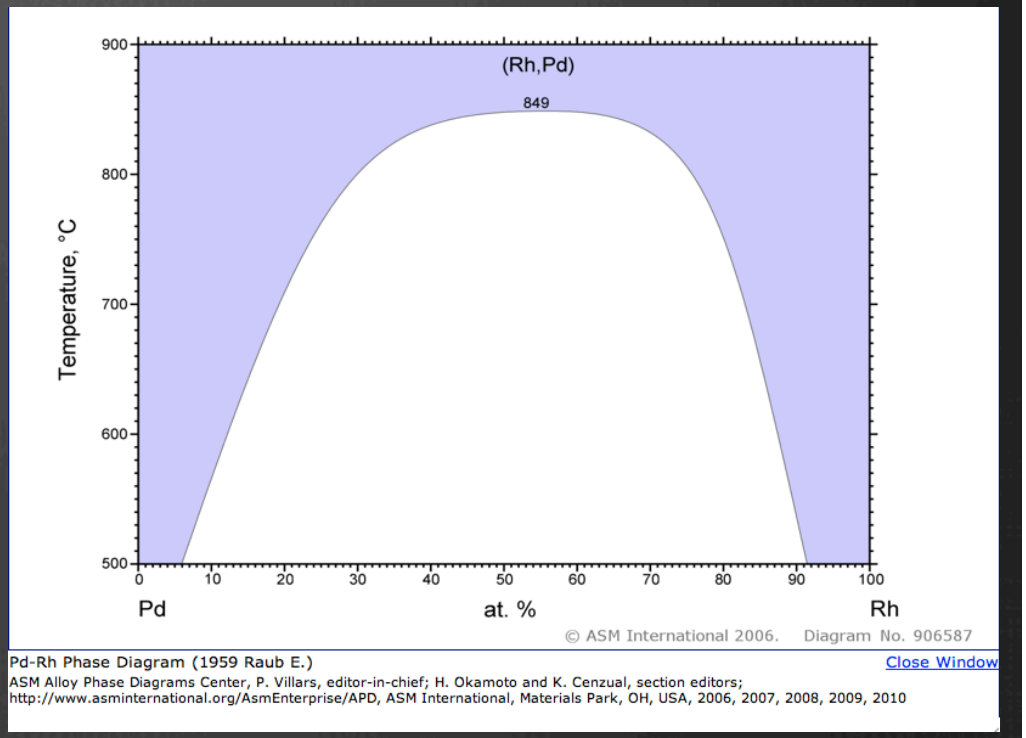
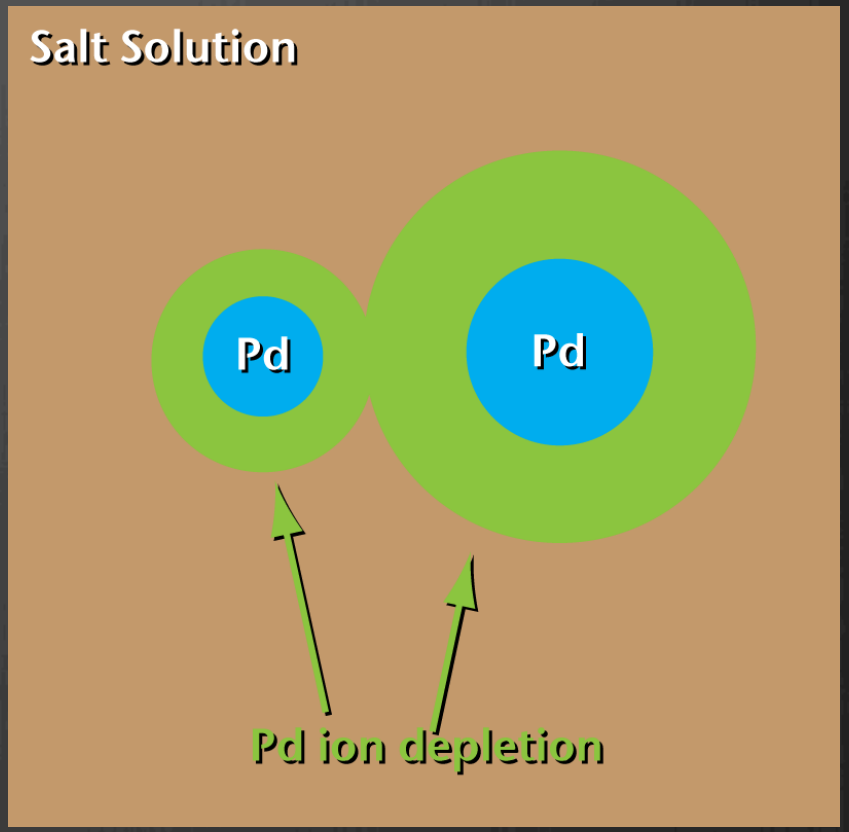


Diffusion-Limited vs. Reaction-Limited Processes

- Averages all seem high (particles ~100 nm)
- Phase diagram suggests Pd-Pd and Rh-Rh bonds preferred
- Competition between diffusion and reaction rates in salt solution
  - Nucleation of Pd-rich particles
  - Formation of Pd-depleted zone



$D_{Pd} > D_{Rh}$

Rate Pd reduction>Rate Rh reduction

Diffusion-Limited vs. Reaction-Limited Processes

- Averages all seem high (particles ~100 nm)
- Phase diagram suggests Pd-Pd and Rh-Rh bonds preferred
- Competition between diffusion and reaction rates in salt solution
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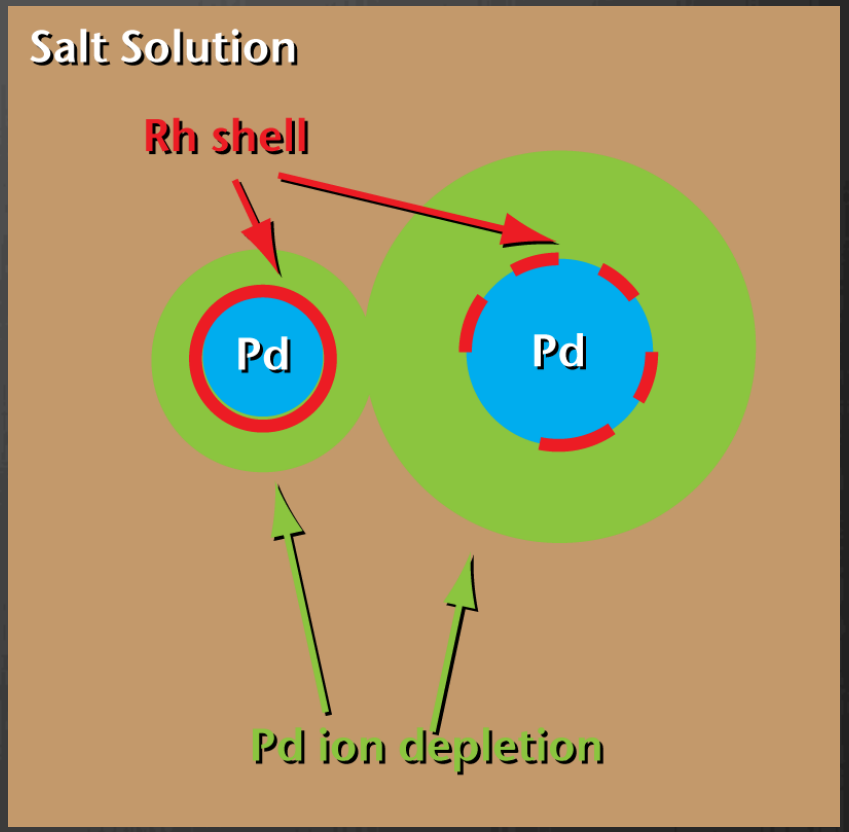
  - Rh reaction dominates
    - Not enough Rh for larger particles



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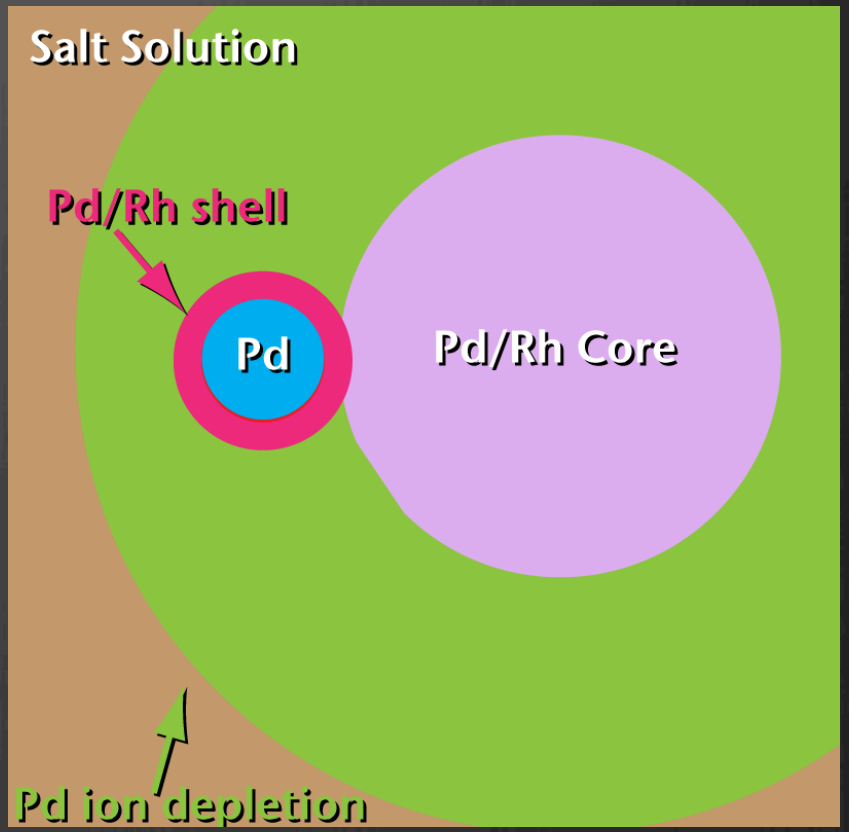
    - Small particle incorporates Rh more readily
    - Large particle alloys at low levels



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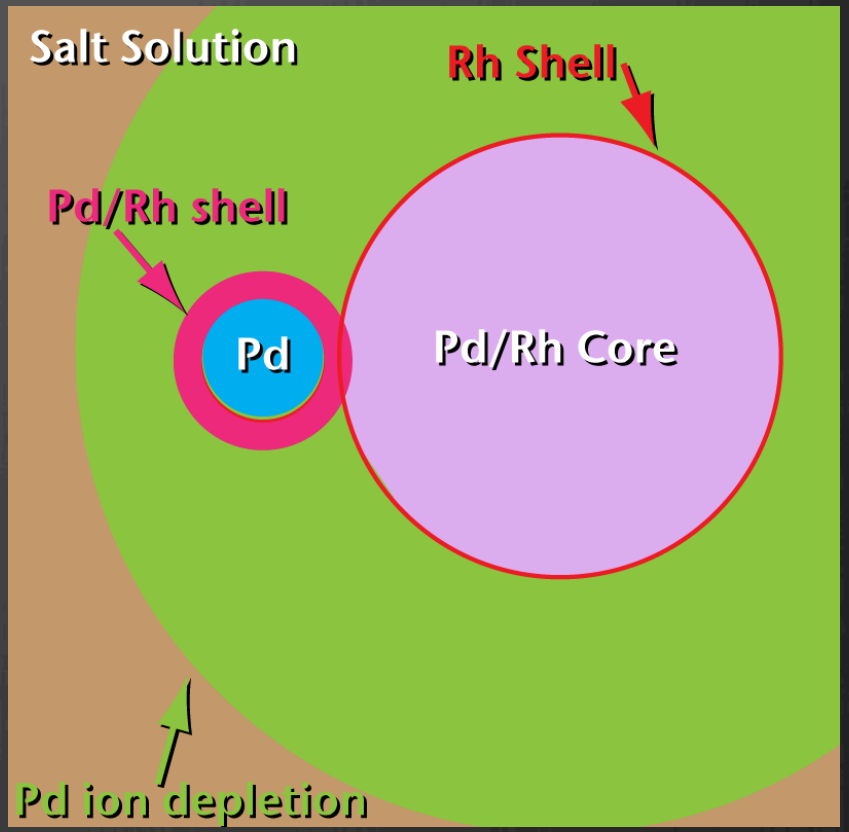

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  - Rh reaction dominates
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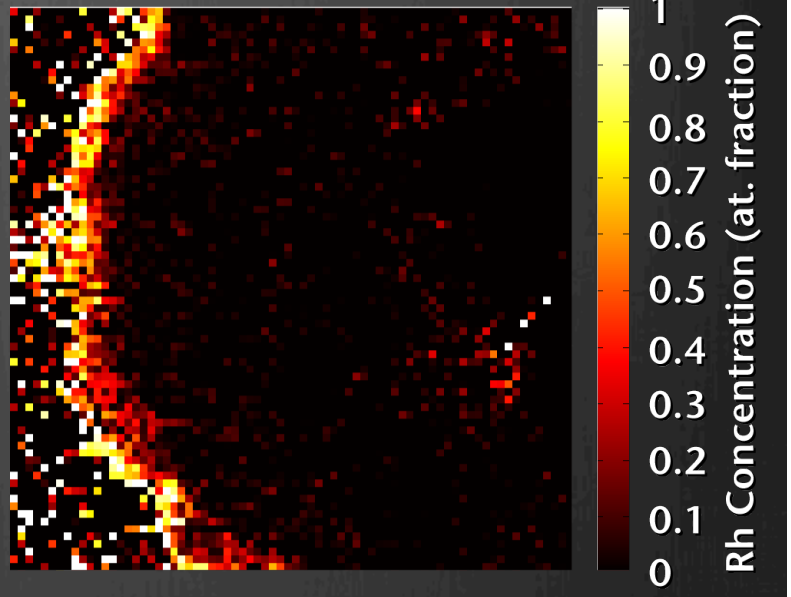
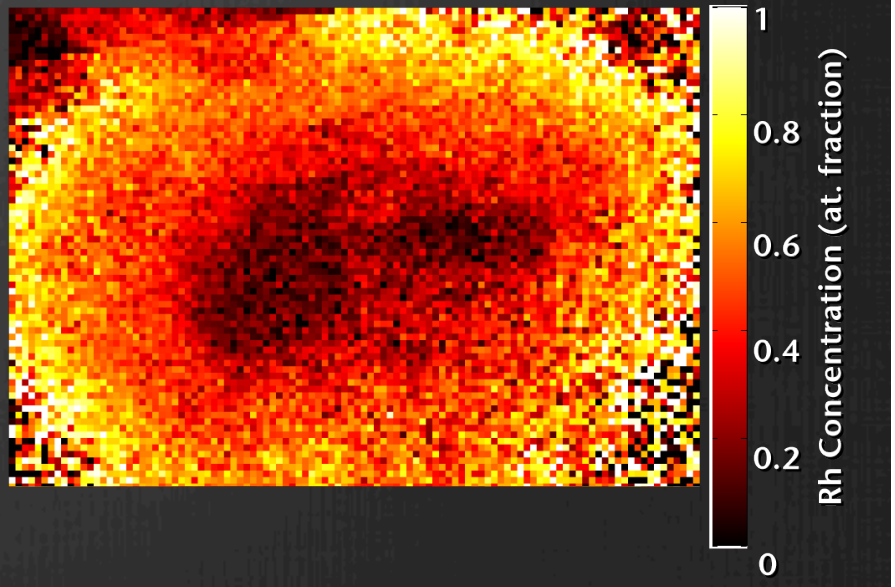
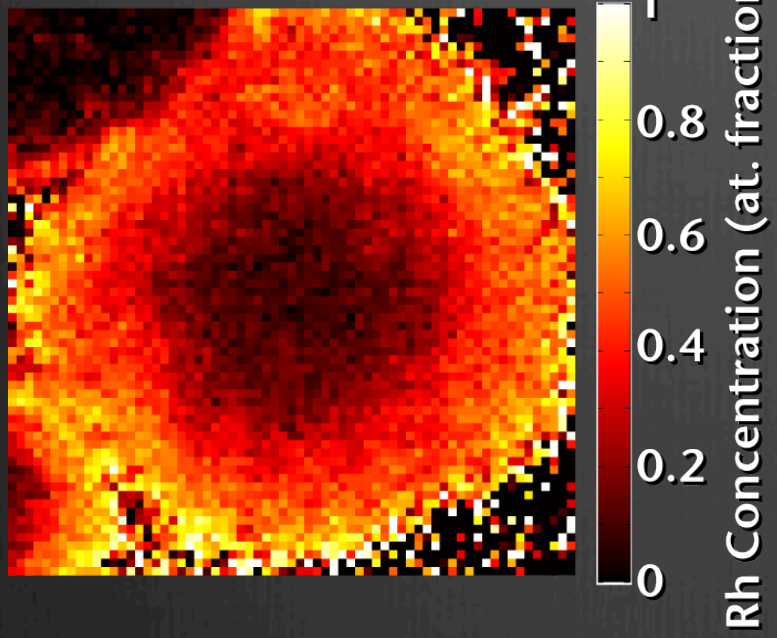
  - Diffusion-limited processes
    - Shell of small particle alloys
    - Core of large particle alloys
  - Pd is consumed so last Rh reduces
- Particle size effects overall Rh distribution



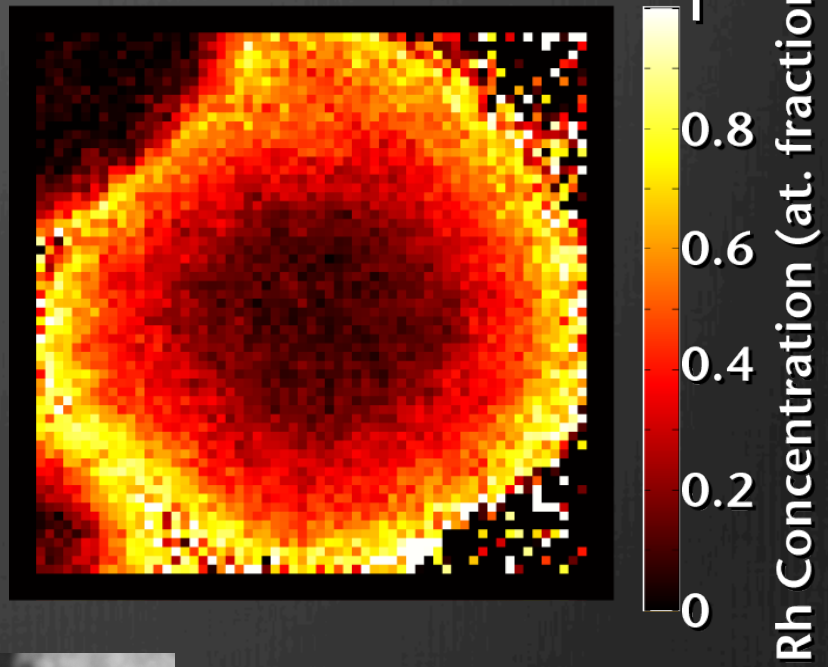


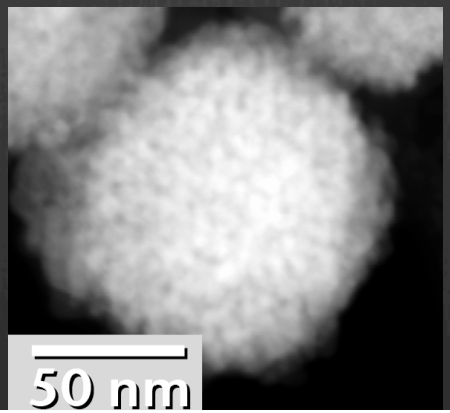
Pd/Rh Surface Rearrangement at High Temperature

After Reduction (H_2) at 300°C



After Oxidation (air) at 300°C





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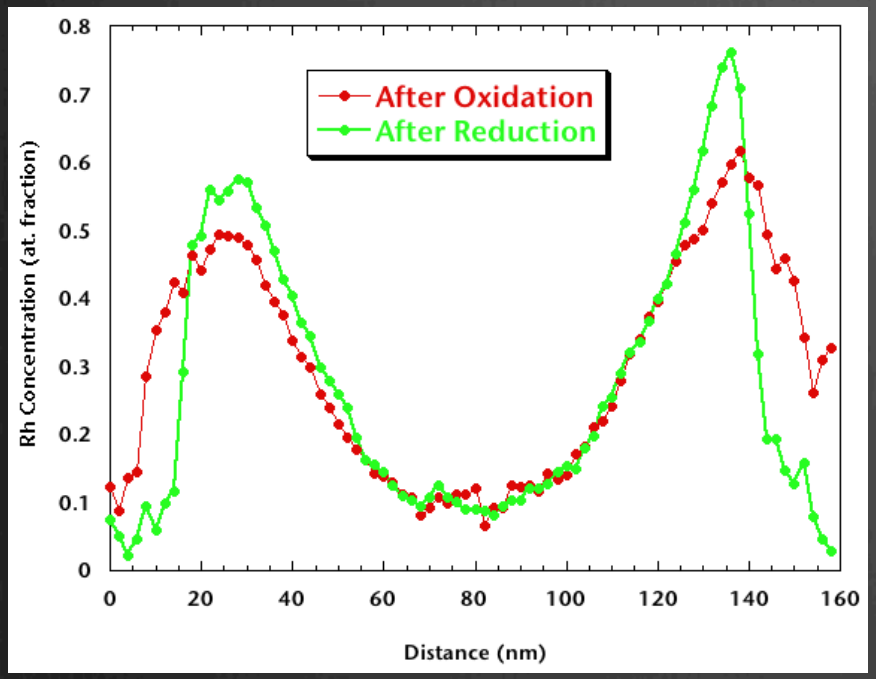
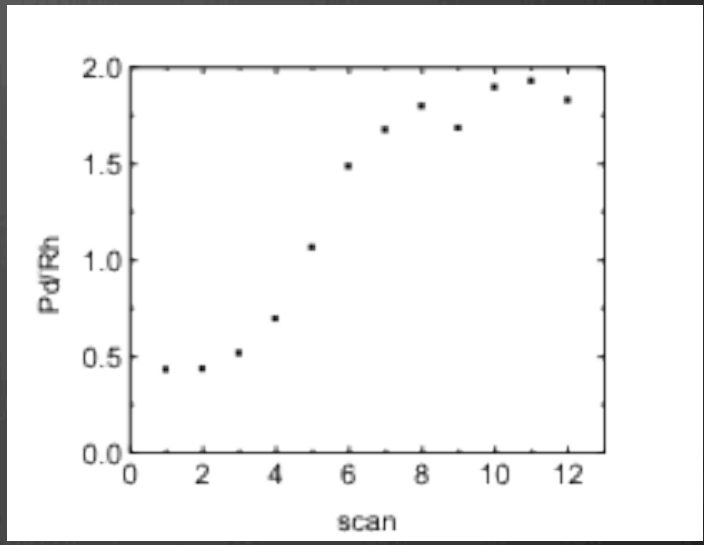
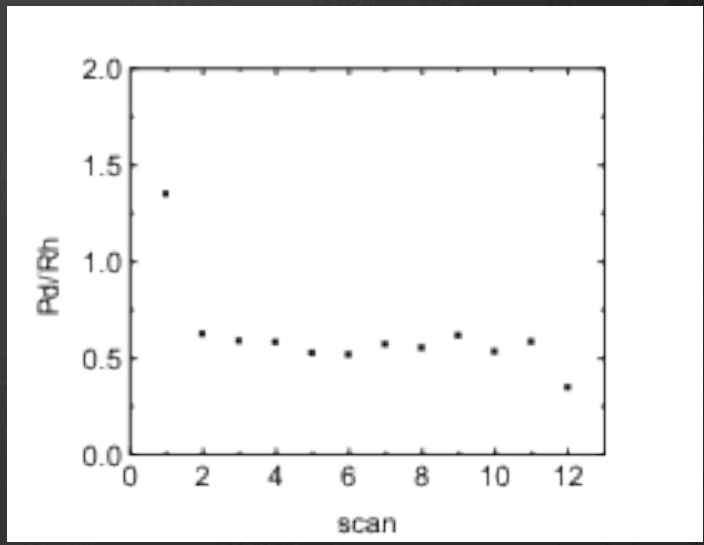




300°C in 100 mtorr H_2



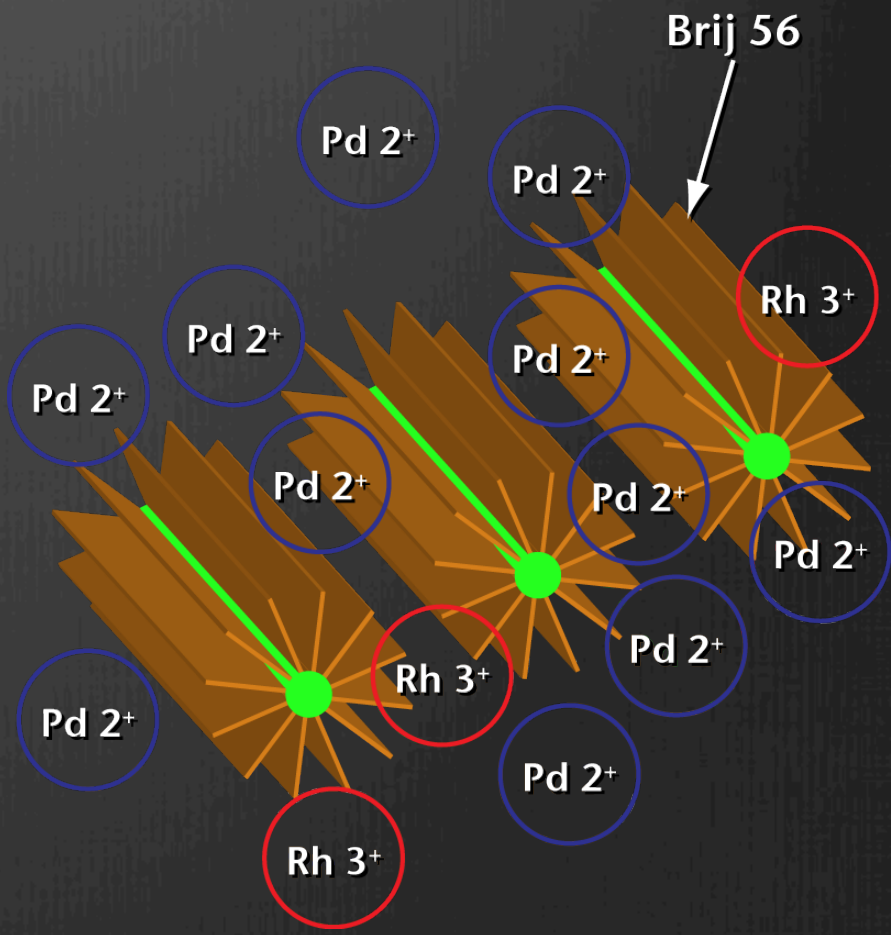
300°C in 100 mtorr O_2

- EDS data shows more enriched Rh surface after oxidation
- This is supported by *in situ* XPS data

Tao et al., *Science* **322**, 2008.
Tao et al. *J Am Chem Soc, **132**, 8697, 2010.*

Summary

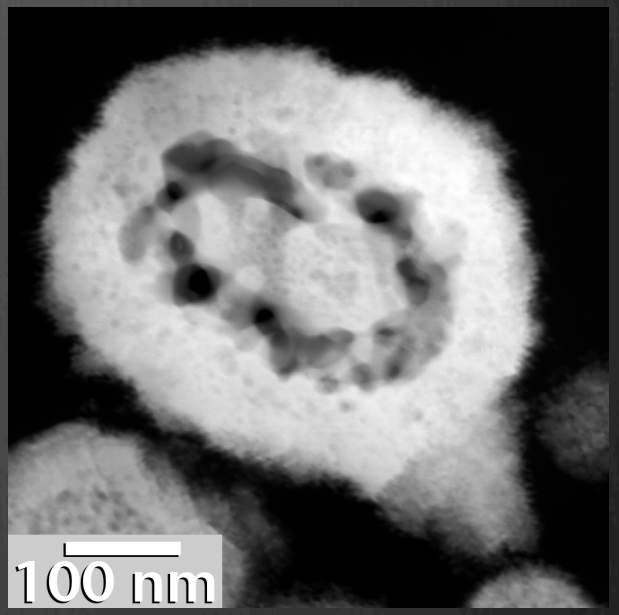
- Surfactant template fabrication of nanoporous Pd/Rh alloys



Summary

- Surfactant template fabrication of nanoporous Pd/Rh alloys
- Non-uniformity in pore size for larger particles
  - More Rh helps

5 at. % Rh



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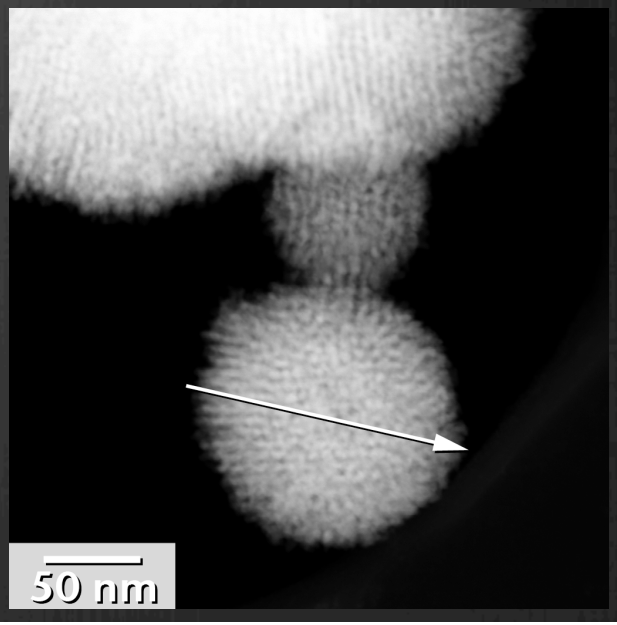

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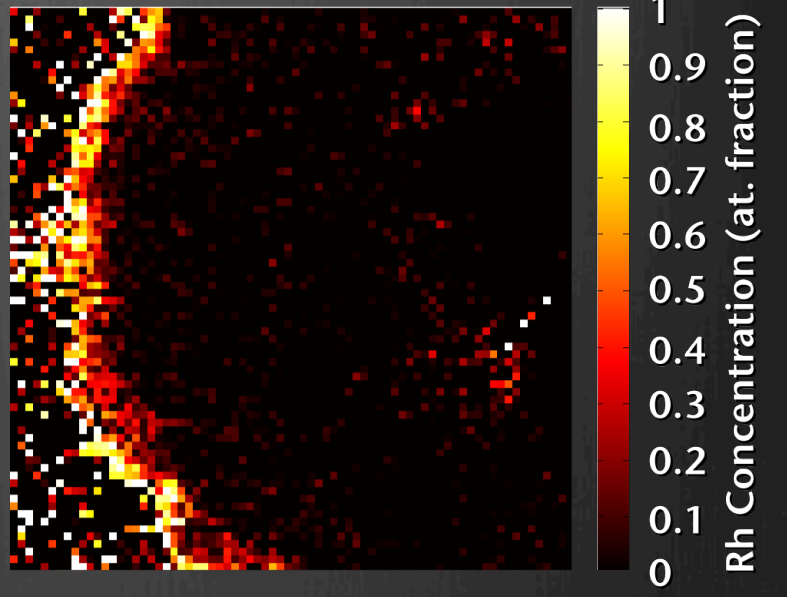

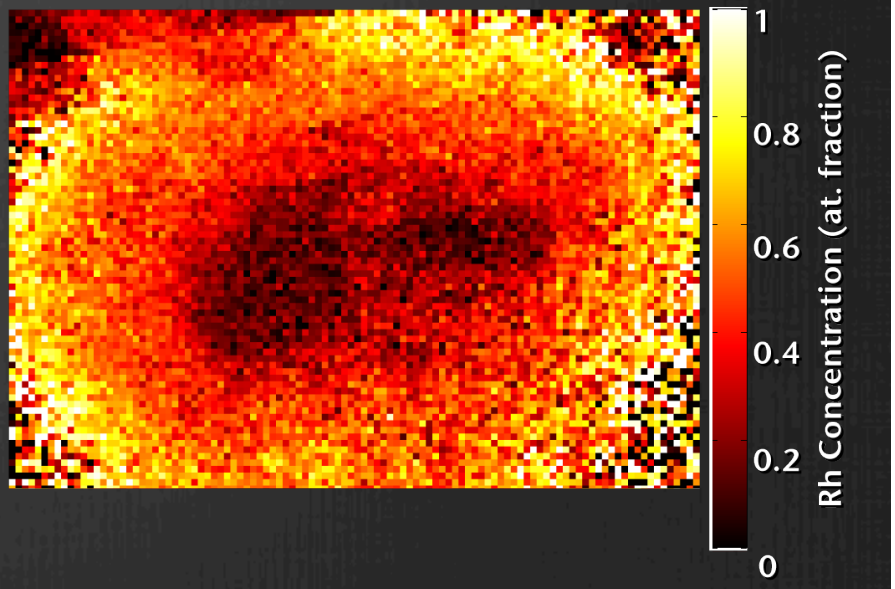

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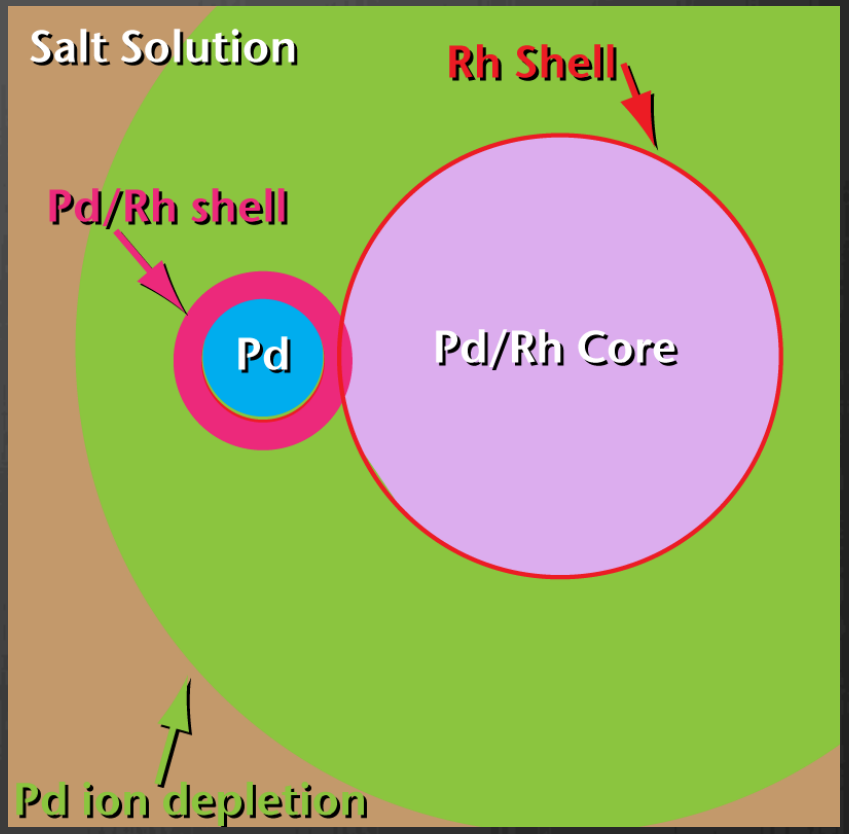
- Diffusion-limited processes cause size dependency in composition profile



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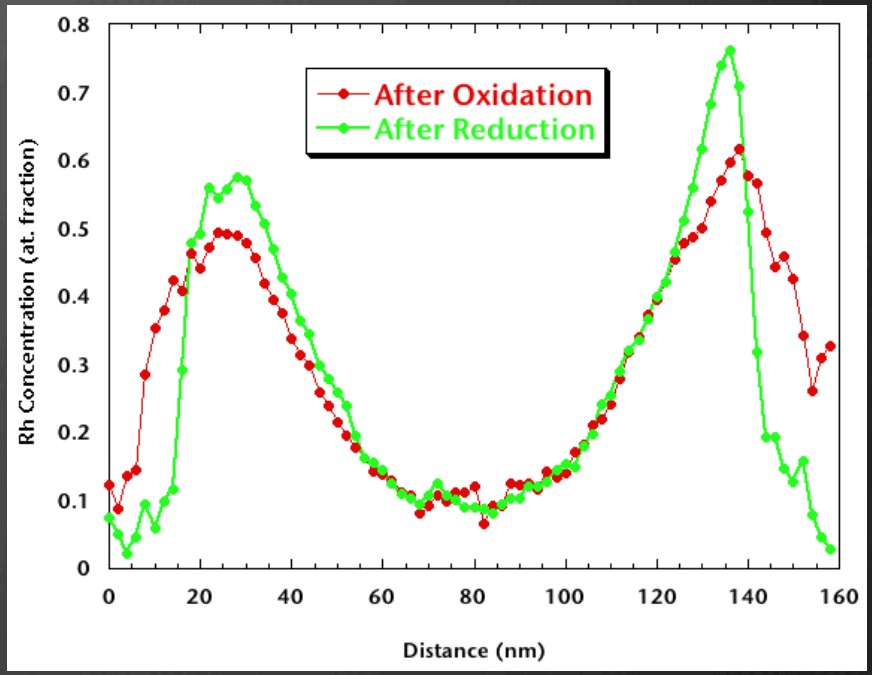
- Rh/Pd flipping at 300°C in H_2/O_2
  - Supported by XPS data



Conclusions

- Nanoporous Pd/Rh alloys are a functional material that show promise as hydrogen isotope storage materials
- Pore structure and composition is not well controlled
- Advanced characterization techniques provide insight into the mechanisms active during formation so that we can attempt to tune the processing parameters for better control
  - More uniform particle sizes could lead to better overall compositional control

Acknowledgements

- Advanced Light Source Staff at LBNL, a DOE user facility
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