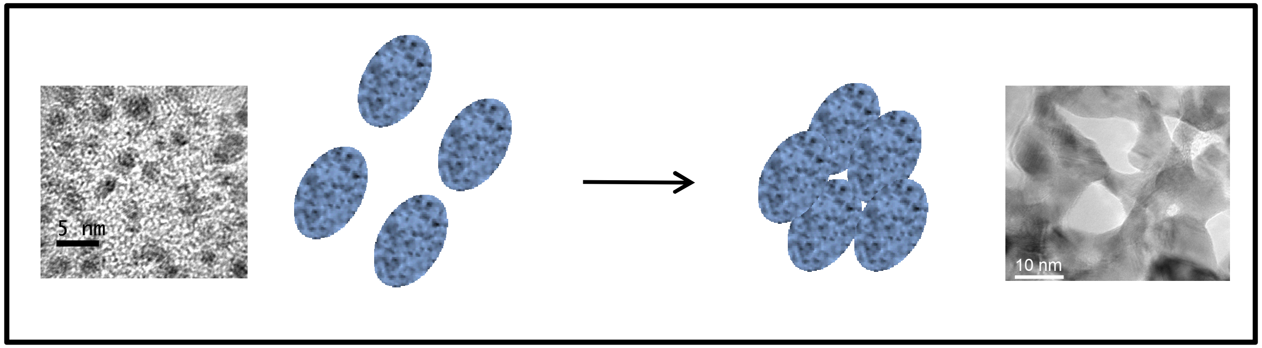
SAND2011-6056C

Nanostructured, nanoporous Palladium alloys from consolidation of dendrimer encapsulated nanoparticles for Hydrogen isotope separation and storage

Patrick J. Cappillino, Michelle A. Hekmaty, David B. Robinson



242nd ACS National Meeting, Denver, Colorado
Division of Colloid and Surface Chemistry
August 28, 2011

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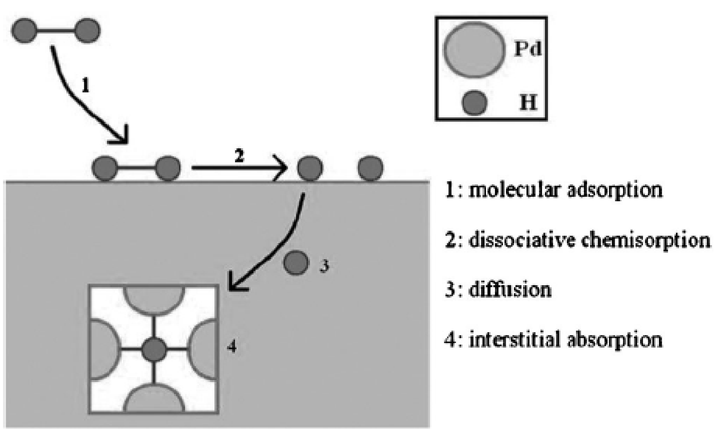
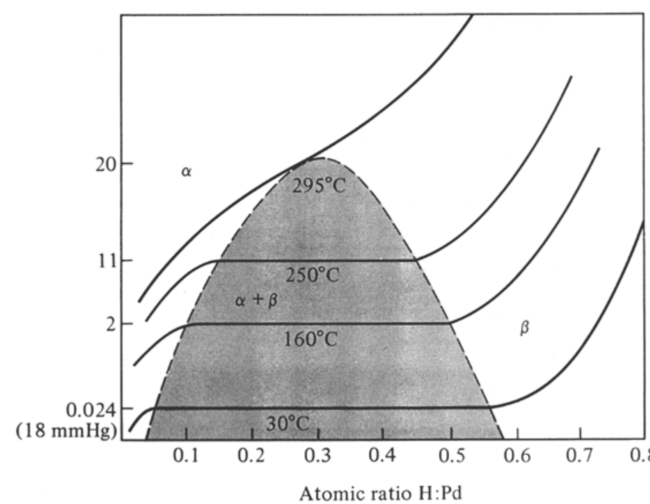
Pd-H System

- Most extensively researched M-H system (~150 y)
- High solubility and mobility of hydrogen in fcc Pd lattice
- H occupies vacant octahedral sites with Pd_2H stoichiometry accompanied by a lattice expansion
- ~0.6 mol H/mol Pd near room temperature at P ~ 10 – 20 mmHg
- Useful in H_2 storage, catalysis, electrochemical, chromatographic/membrane isotopic separations
- Very expensive, limited to high-value applications such as hydrogen isotope storage

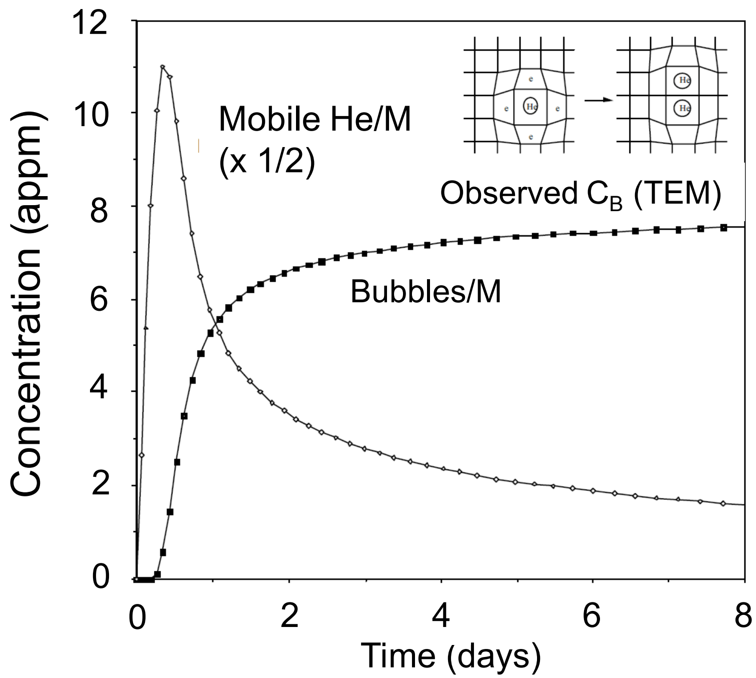




Delmelle, R; Proost, J., Phys. Chem. Chem. Phys. (2011) p.11412
Knapton, A.G., Platinum Metals Reviews (1977) p. 44

Desirable Aspects of Nanoporous Pd and Pd alloys:

- More rapid H_2 transport than bulk (Chromatography)
- High surface area for electrochemical applications
- Greater tolerance to volume change
- In particular, hypothesized to stabilize Pd-^{3}H



$^3H \rightarrow {}^3He + e^- +$ anti-neutrino

- ^{3}He near surface diffuses away
- ^{3}He in bulk metal nucleates to form bubbles that distort the metal lattice
- ^{3}He clusters expand and eventually force ejection of metal atoms
- In nanoporous metals all sites are near surface

Cowgill, D., Fusion Science and Technology, 28 (2005) p. 539

Porous Pd and Pd alloys:
State of the Art and Targets for Improvement

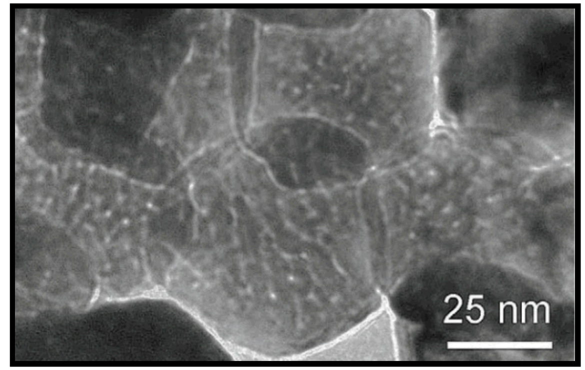
Pd and $Pd_{0.9}Rh_{0.1}$ alloys with 2 nm pores:

- Prepared by surfactant-templated approach
- Lack of pore regularity observed in pure Pd/Pd-rich samples leads to suboptimal surface area
- Pore collapse at ~150 C in pure Pd
- Alloys show improved thermal stability (~400 C) but inhomogenous Rh distribution
  1) Kinetics of reduction
  2) Within miscibility gap

Goals for improved material:

- Higher surface area (50 m^2/g ~ 100% of metal atoms within 2 nm of surface)
- Uniform composition→ uniformly stable
- Better control of nanoscale composition (Rh at the surface) – control thermodynamics and kinetics of hydriding

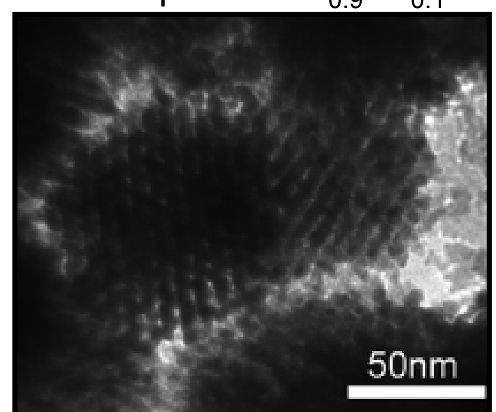
Robinson, D.B.; Int. J. Hydrogen Energ. 34 (2009), p. 5585



mesoporous Pd

Surface area =16 m^2/g

mesoporous $Pd_{0.9}Rh_{0.1}$



Surface area = 20 m^2/g

Robinson, D.B.; Int. J. Hydrogen Energ. 35 (2010), p. 5423

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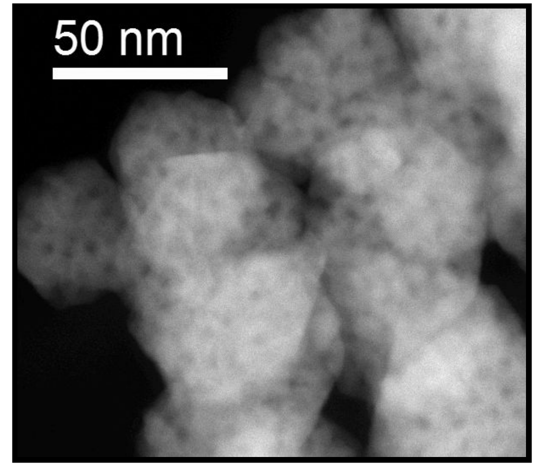
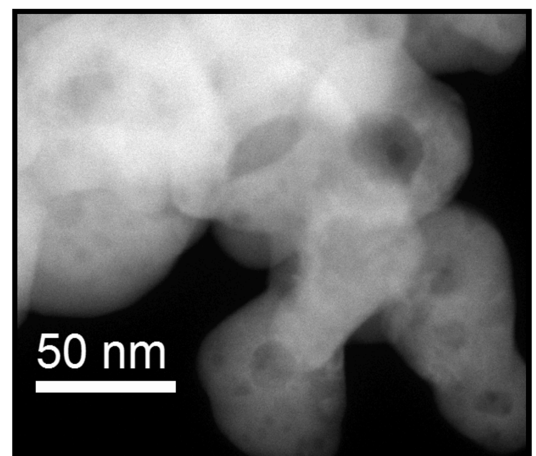


50 C

mesoporous Pd



150 C

Arslan *et al*., J. Am. Chem. Soc. (2011), p. 9144

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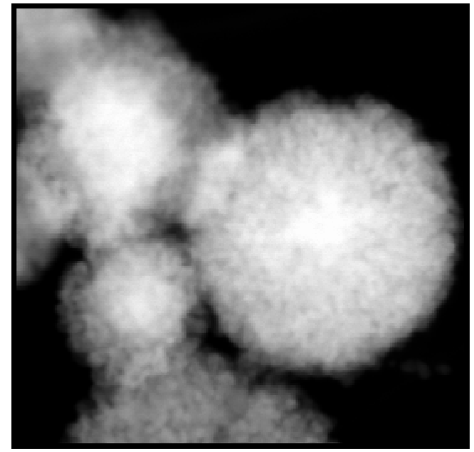
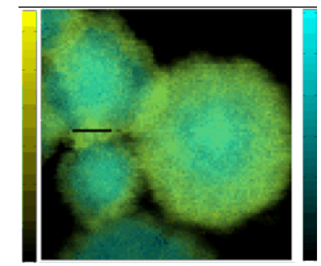
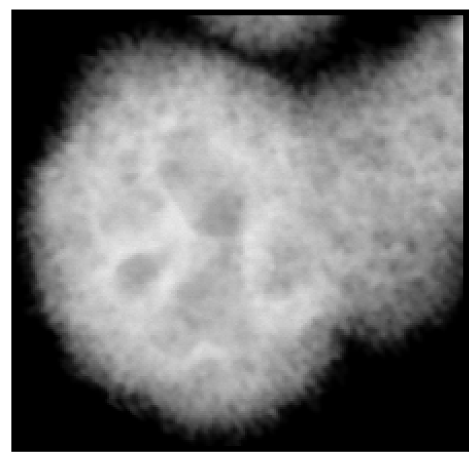


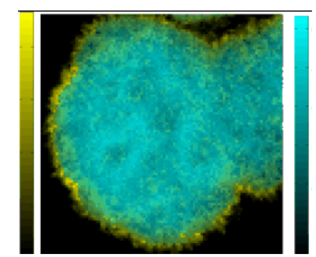
Spectral Imaging

Rh Pd



Mesoporous $Pd_{0.9}Rh_{0.1}$, 200°C





Ong *et al.*, in submission

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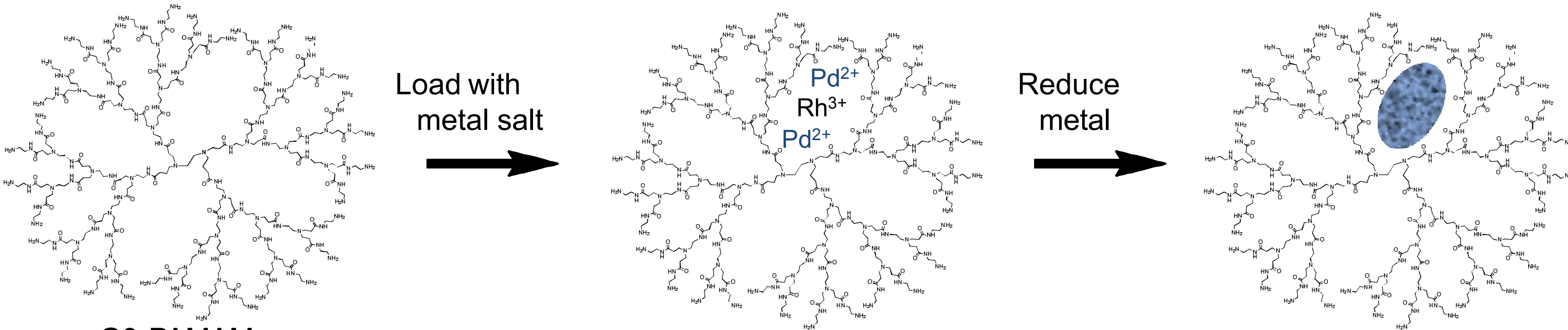
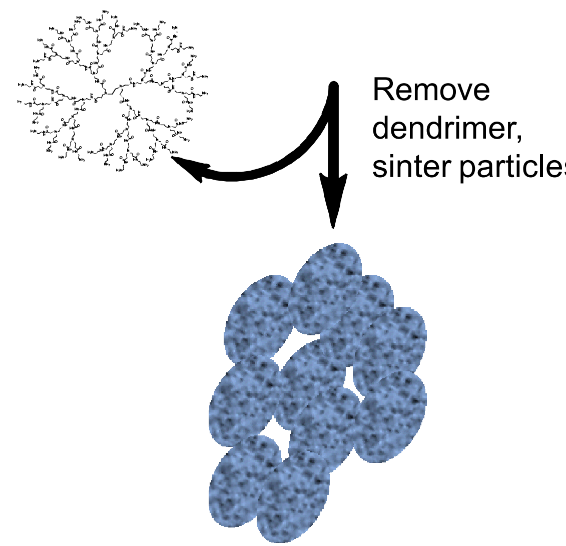
Dendrimer Encapsulated Nanoparticles (DEN)



G3-PAMAM

- Dendrimers are commercially available, highly branched, organic polymers
- Addition of metal salts → coordinate to interior tertiary amines
- Reduction of metal yields uniform ~1-3 nm NP
- Removal of dendrimer causes sintering of NP → porous material
- Uniform NP composition → uniform sintered material composition
- Core/shell NP → segregation of metals at small scale with uniformity at larger scale



Porous network of fused nanoparticles

Scott, Robert W. J;Wilson, Orla M.; Crooks, Richard M., *J. Phys. Chem. B* (2005), 692-704

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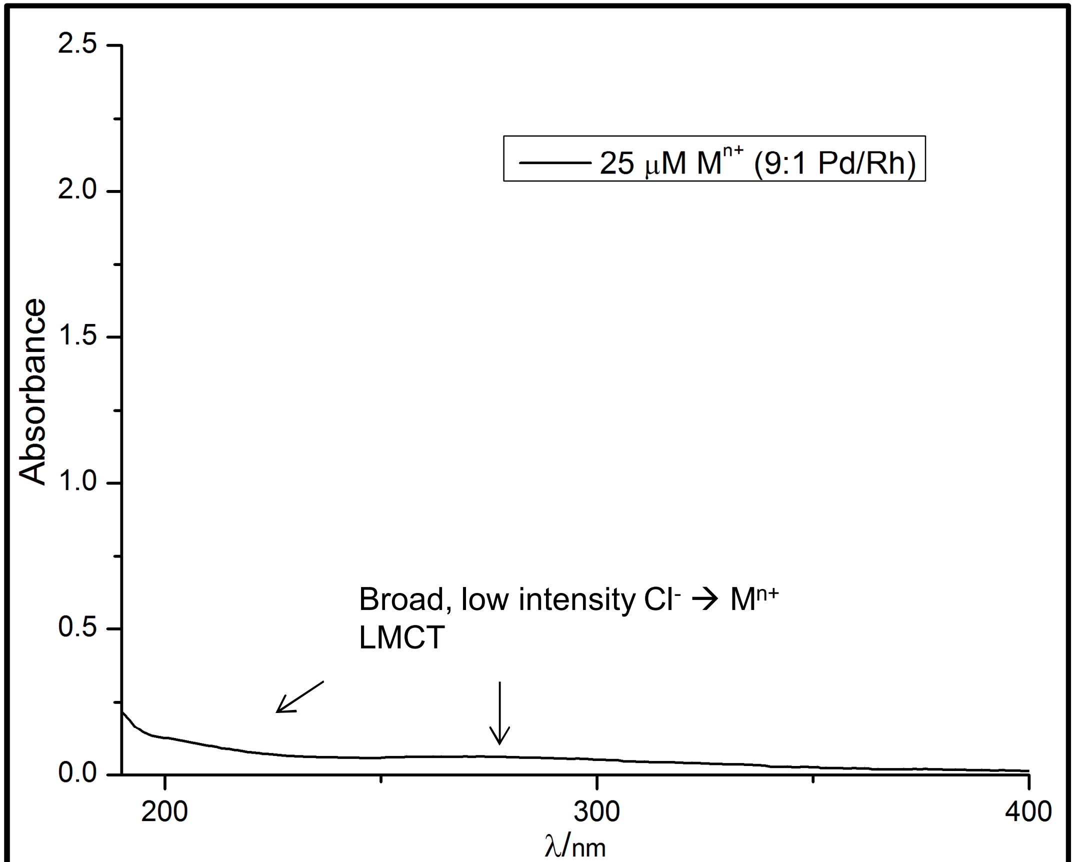
Synthesis of DEN:
G3-$Pd_{0.9}Rh_{0.1}$



Synthesis of DEN followed by UV/vis spectroscopy:

- ➢ *absorbance of aqueous metal salts (K_2PdCl_4 and $RhCl_3$) at ~210 nm and ~280 nm*
- Addition of metal salt solution to dendrimer solution, more intense chromophore, ~240 nm
- Reduction of metal with $NaBH_4$ (10 eq.), disappearance at ~240 nm, intense feature at ~200 nm

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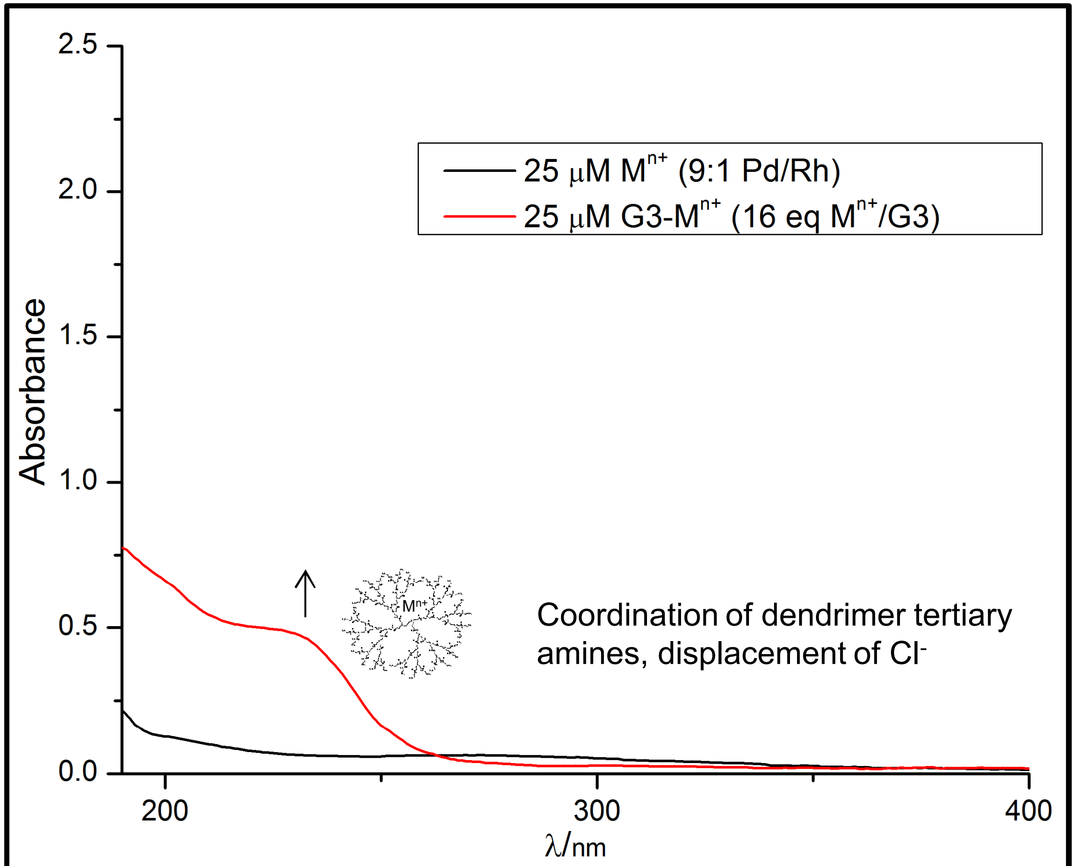

Pd^{2+}/Rh^{3+} + G3-PAMAM ⟶ G3-$Pd^{2+}{}_{0.9}Rh^{3+}{}_{0.}$

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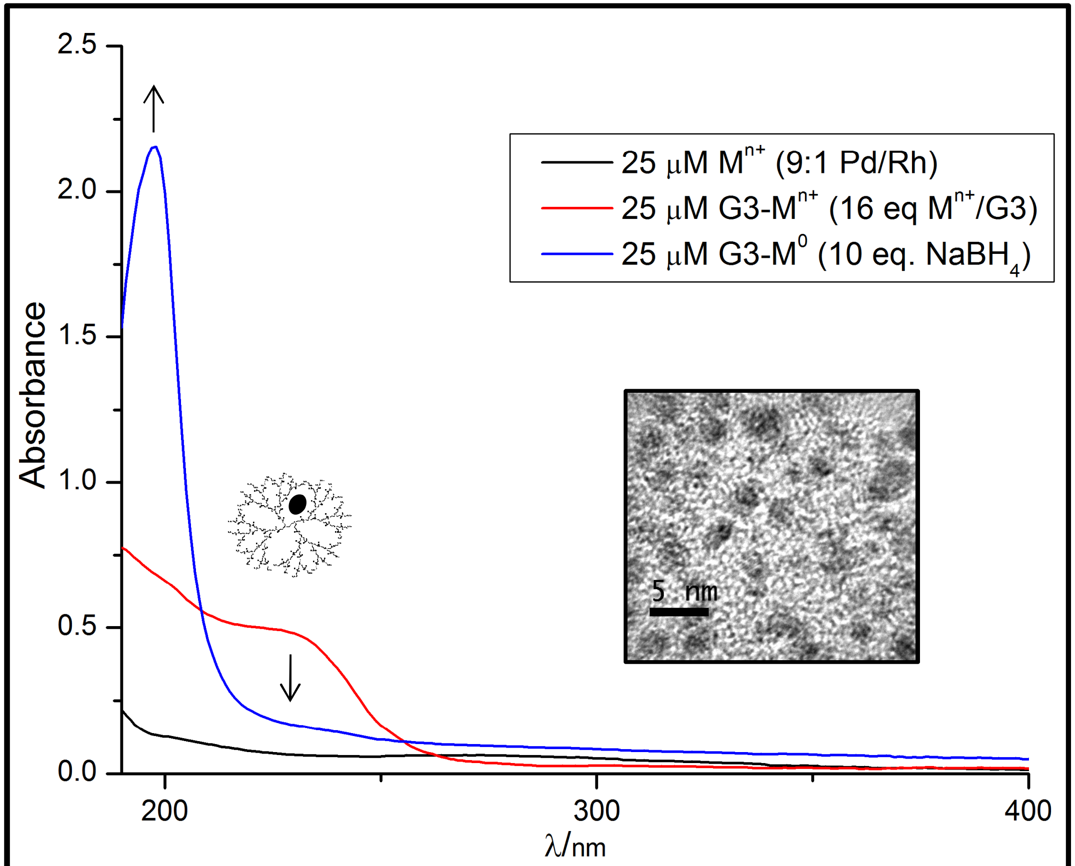

G3-$Pd^{2+}_{0.9}Rh^{3+}_{0.1}$ $\xrightarrow{NaBH_4}$ G3-$Pd_{0.9}Rh_{0.1}$

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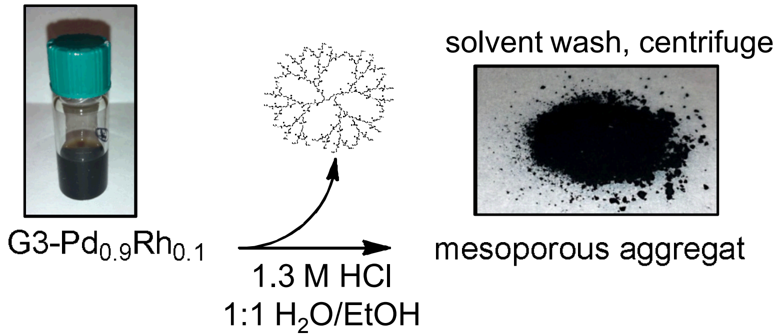
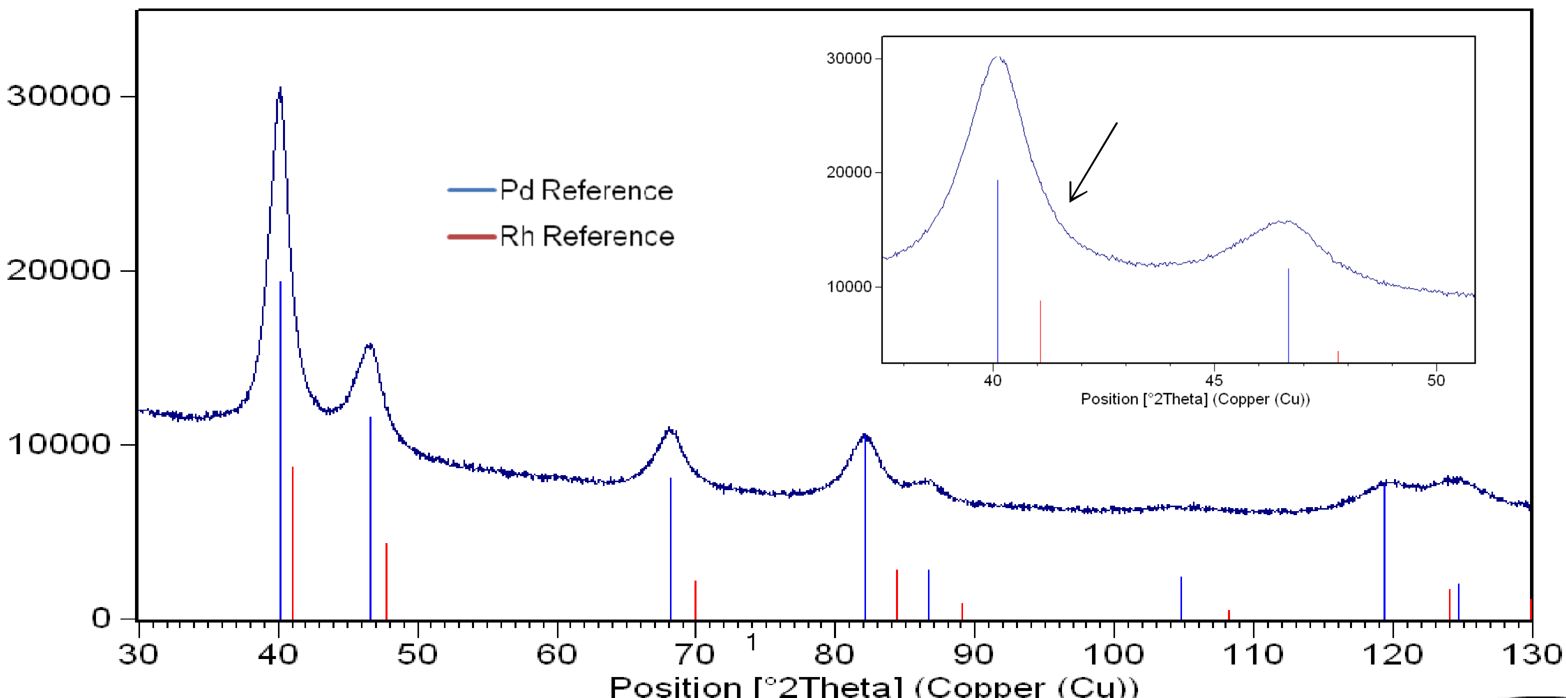
Mild Sintering Step:
Low pH Removal of Dendrimer



- pH < 2 destabilizes colloidal suspension
- Protonated interior and terminal amines have no interaction with nanoparticles
- 85-90% of dendrimer removed by washing (6-7 wt % remains, by TGA)
- Powder XRD consistent with 4-5 nm crystallites, no pure Rh phases



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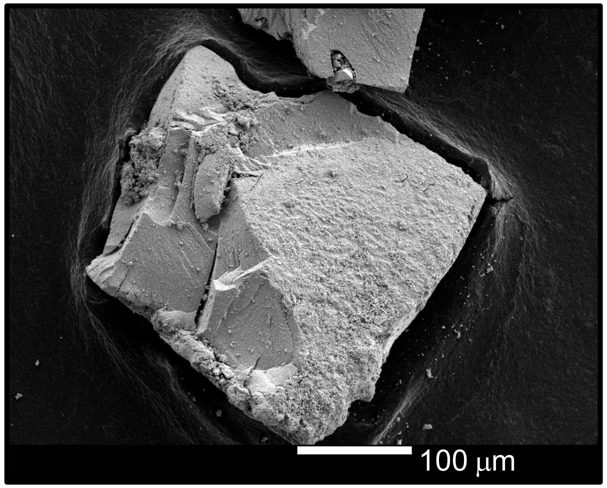
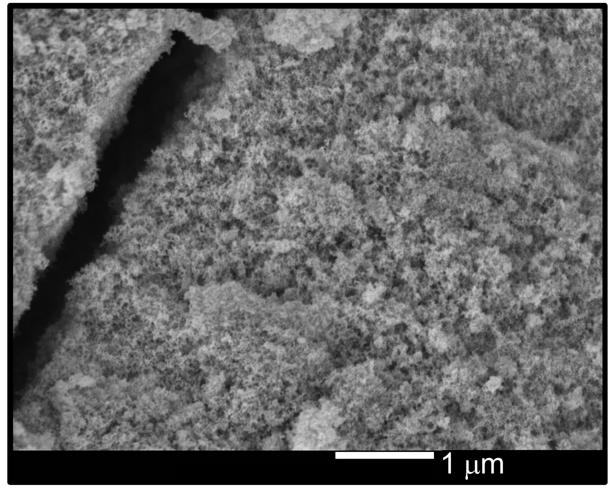
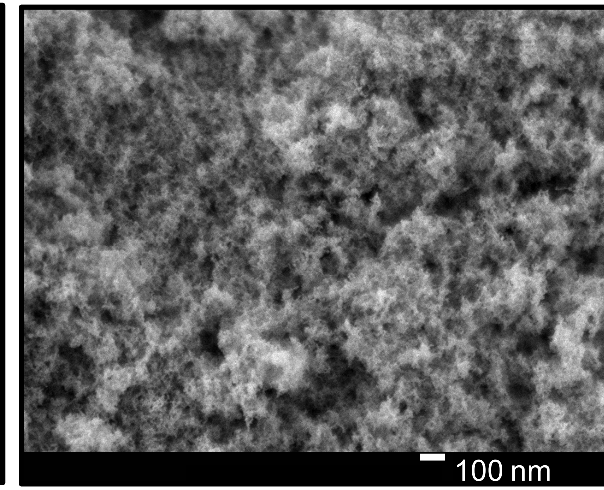
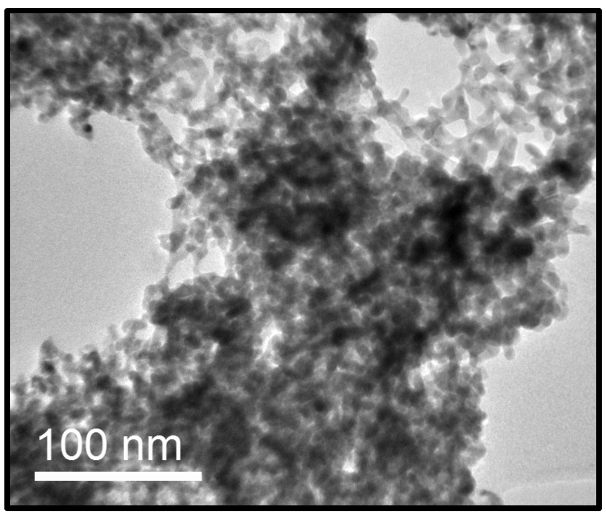
Electron Microscopy

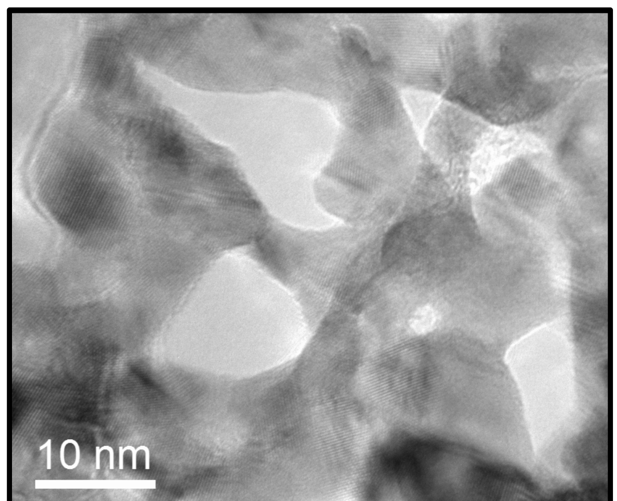
G3-$Pd_{0.9}Rh_{0.1}$





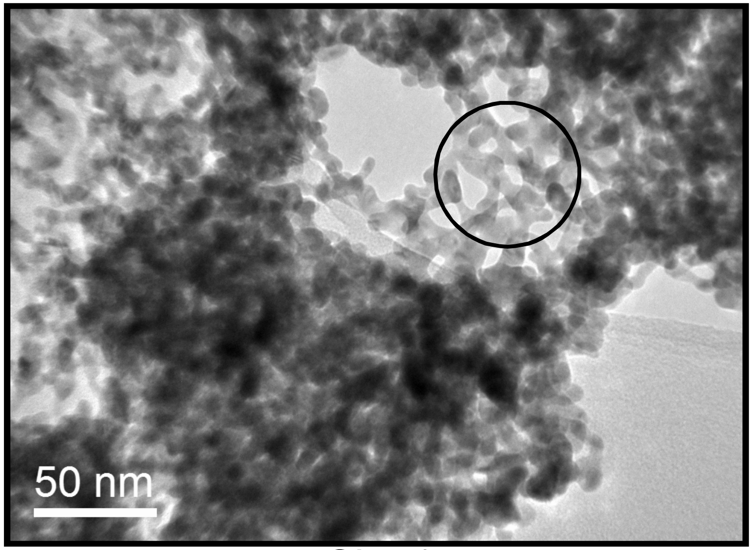




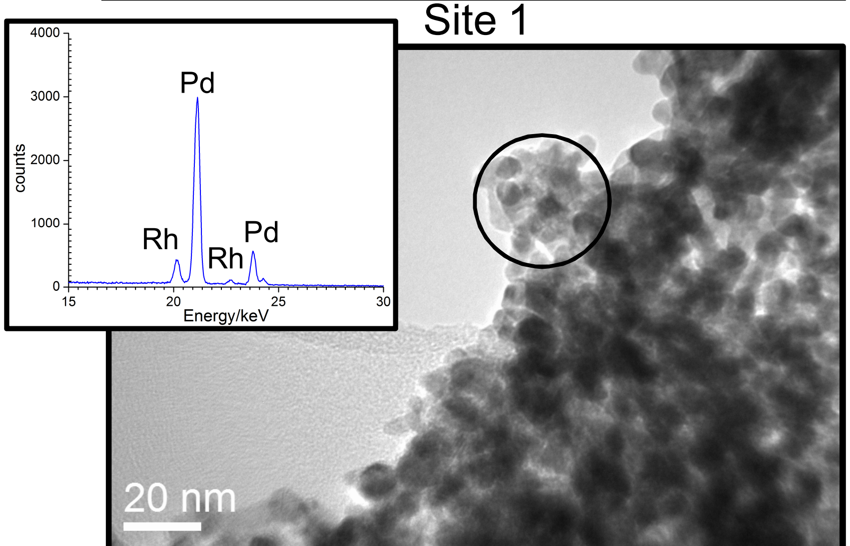


- Low Magnification:
  - Porous/sponge-like
  - Very large particles
- High Magnification:
  - hard sintering gives rise to 5-10 nm ligaments
  - broad pore size distribution

Compositionally Uniform Sintered Material



Site 1



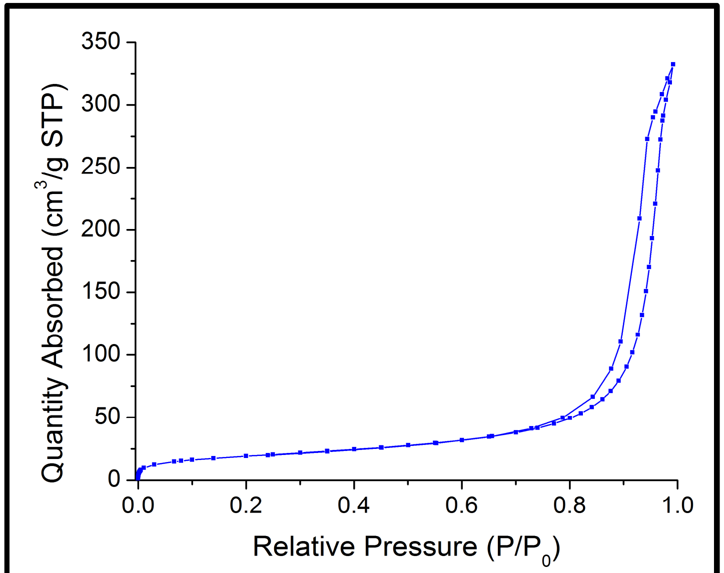
Site 2

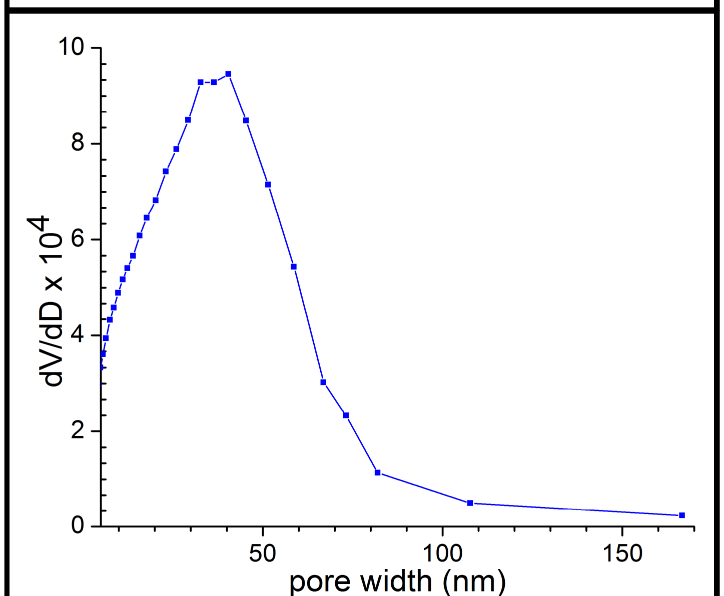
- All EDS spectra show composition within 1% of nominal
- XPS → large area sampled, within 1% of nominal
- Key aspect for reliable, predictable H-storage properties
- *Prediction*: thermally stable pore structure throughout

	Pd (wt %)	Rh (wt %)
Site 1	90.4	9.6
Site 2	91.0	9.0
XPS	89.8	10.2
Nominal	90.9	9.1

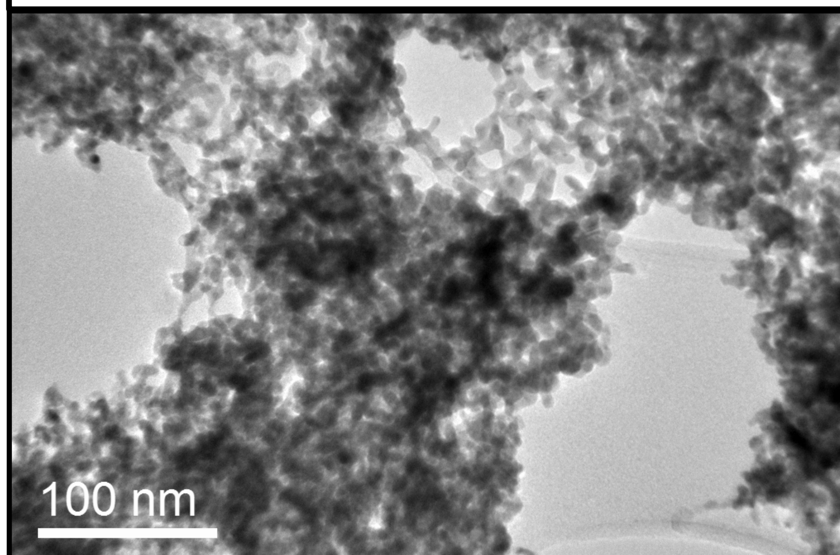
Nitrogen Porosimetry

G3-$Pd_{0.9}Rh_{0.1}$





- Bulk measurement provides generally good agreement with microscopy
- Mesoporous, high specific surface area: 68 m^2/g (BET)
- High pore volume: 0.5 cm^3/g (BJH & single point)
- Most of pore volume b/n 20 and 60 nm, peak near 40 nm
- Average pore diameter: 22-26 nm



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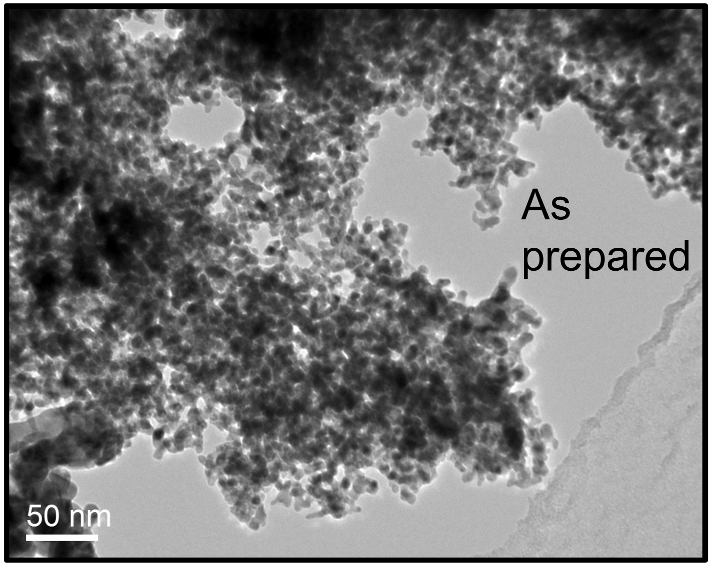
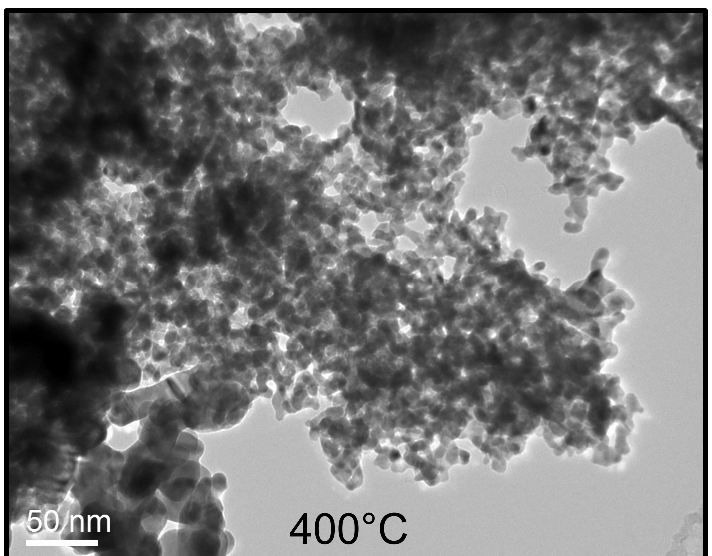
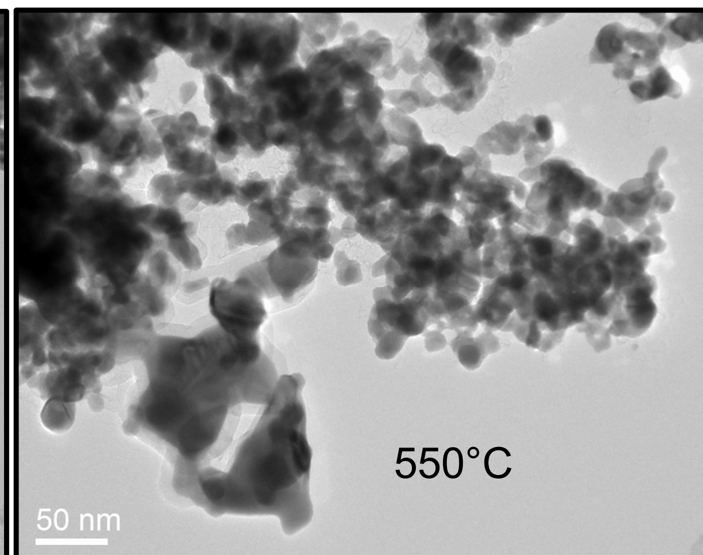
In situ heating

G3-$Pd_{0.9}Rh_{0.1}$



- Pore structure intact to 400°C
- No low temperature collapse indicative of pure Pd
- Both alloying metal and larger average pore size contribute to more stable pores
- Suggest removal of residual organic material (200-250°C) is possible without collapse of pores





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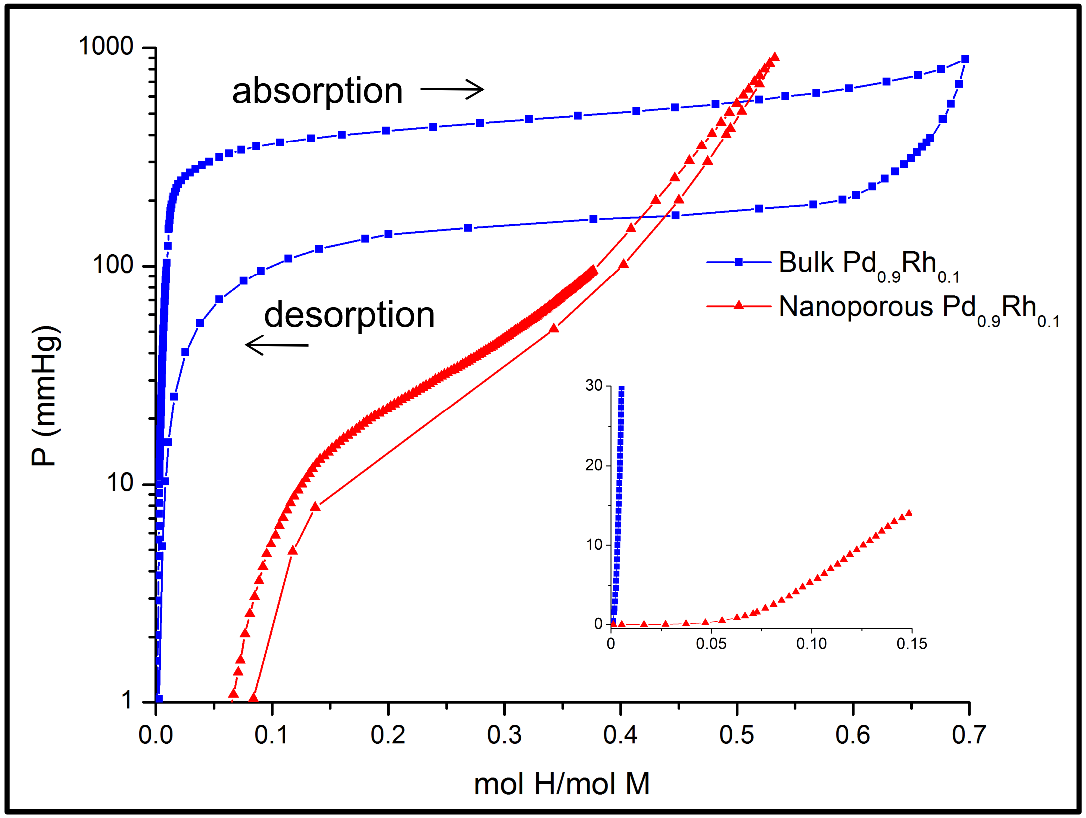
H_2 Storage Properties

G3-$Pd_{0.9}Rh_{0.1}$



- Nanoporous material has somewhat lower H_2 capacity than bulk (~1 micron PS)
- Sloping P_{plat} similar <10 nm Pd NP
- Low P storage is higher than bulk (crossover ~ 0.5 mol H/mol M)
- Considerably less hysteresis → pore volume facilitates volume change
- Significant surface adsorption of H_2 in porous material, not in bulk

$$1/_2\ H_2\ (g) \rightleftharpoons \beta\text{-PdH}\ (s)$$

Bulk $Pd_{0.9}Rh_{0.1}$ provided by N. Yang

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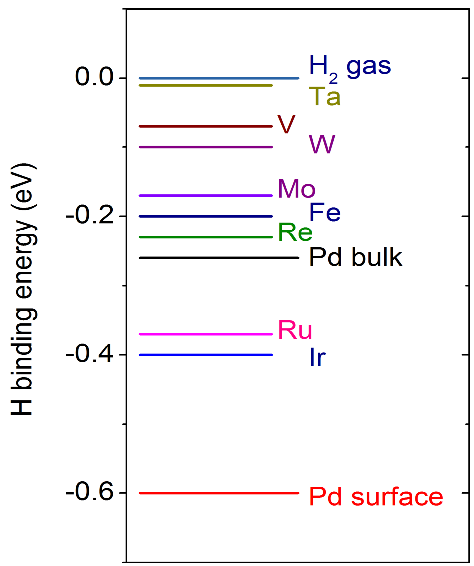
Nanostructured Material:
Rh at pore surfaces

Motivation:

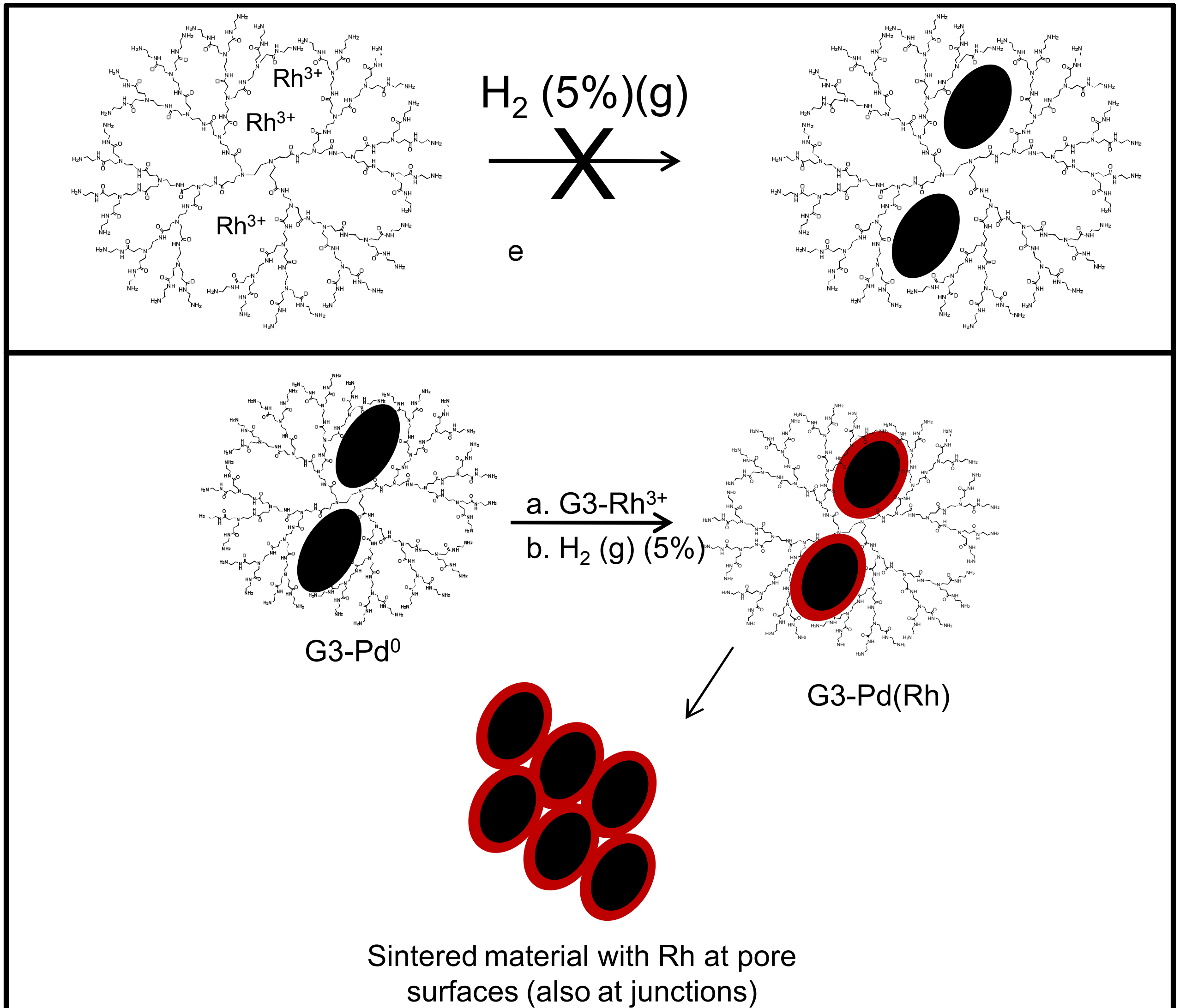
- Surface Rh may impart thermal stability
- Effect on thermodynamics of H_2 storage (more Pd-like PCT)
- Kinetics of hydriding affected by surface, subsurface alloy



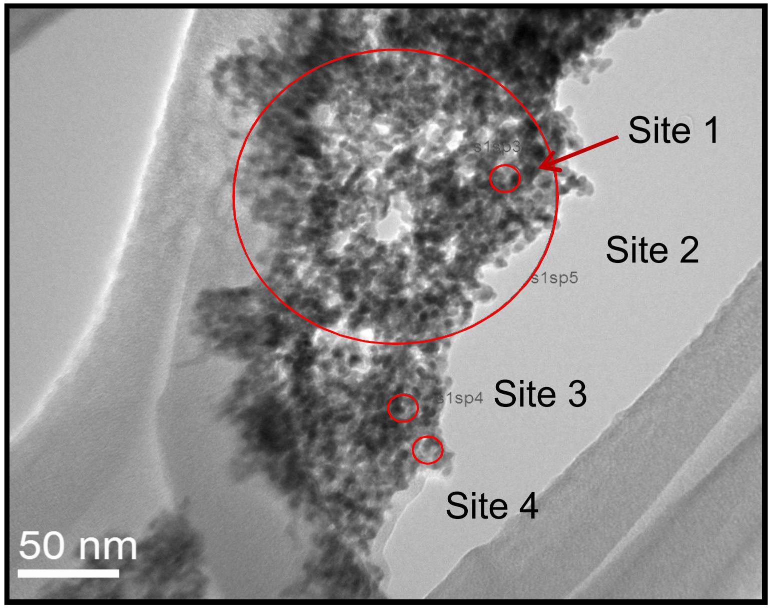
Greeley, J. and Mavrikakis, M., J Phys Chem B 2005, p. 3460

Stability of surface hydride should affect barrier to hydrogen absorption

Strategy for Synthesis



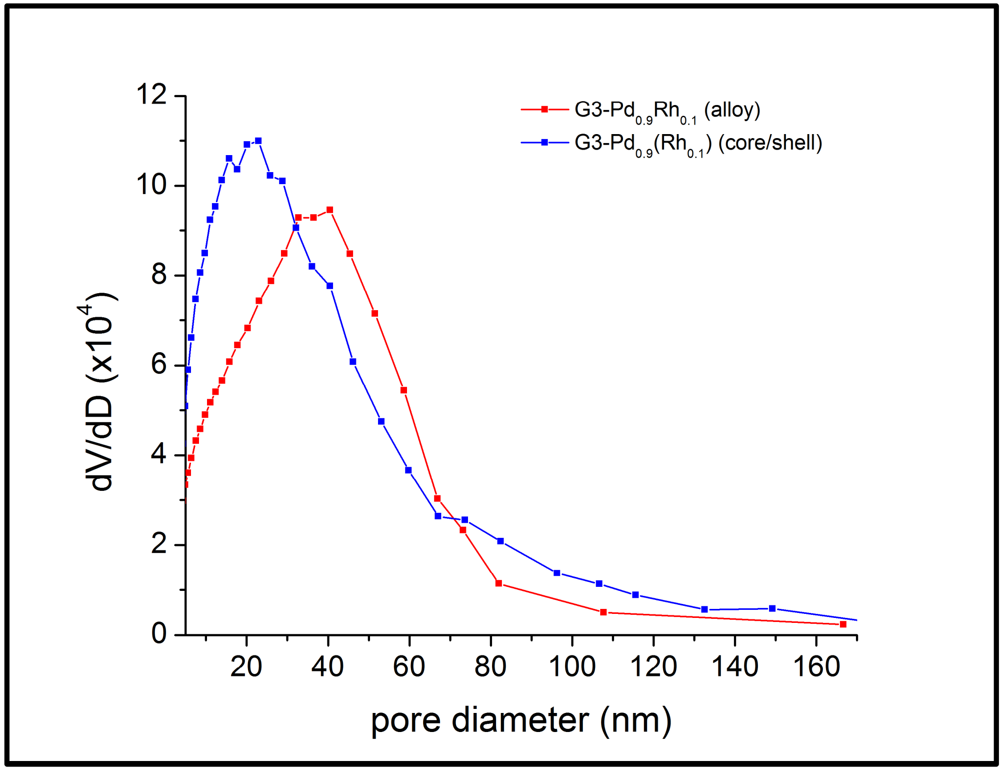
Elemental Analysis
G3-$Pd_{0.9}(Rh)_{0.1}$

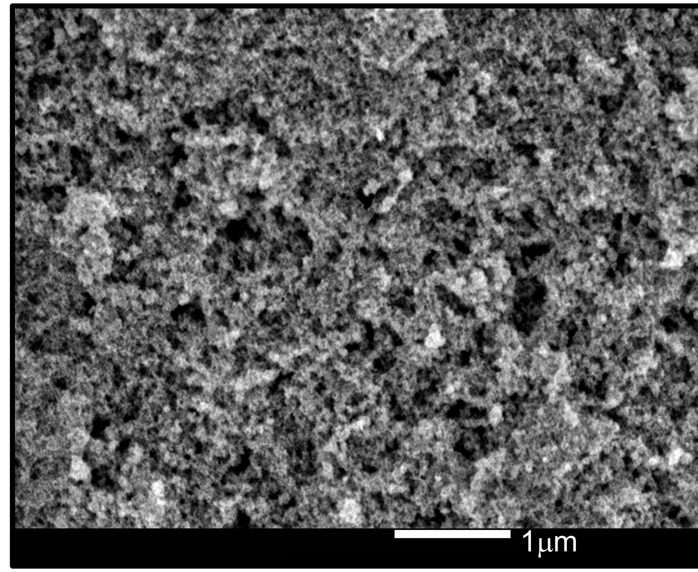


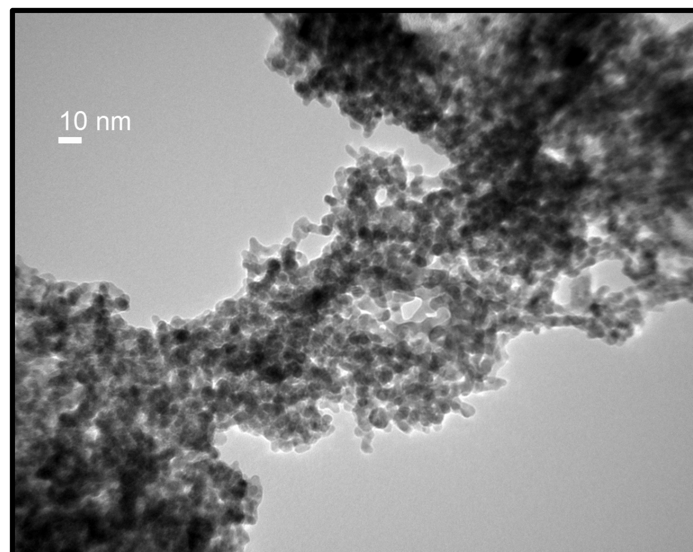
	Pd (wt %)	Rh (wt %)
Site 1	95	5
Site 2	93	7
Site 3	93	7
Site 4	98	2
SEM	90	10
XPS	91	9
Nominal	91	9

- Close to nominal composition at large scale (SEM, XPS)
- Somewhat inhomogeneous at small scale
- Consistent with some segregation of Rh

Characterization of G3-$Pd_{0.9}(Rh)_{0.1}$ (Core/shell)







- 83 m^2/g surface area
- Morphology very similar to alloy
- Pore Size Distribution similar to alloy

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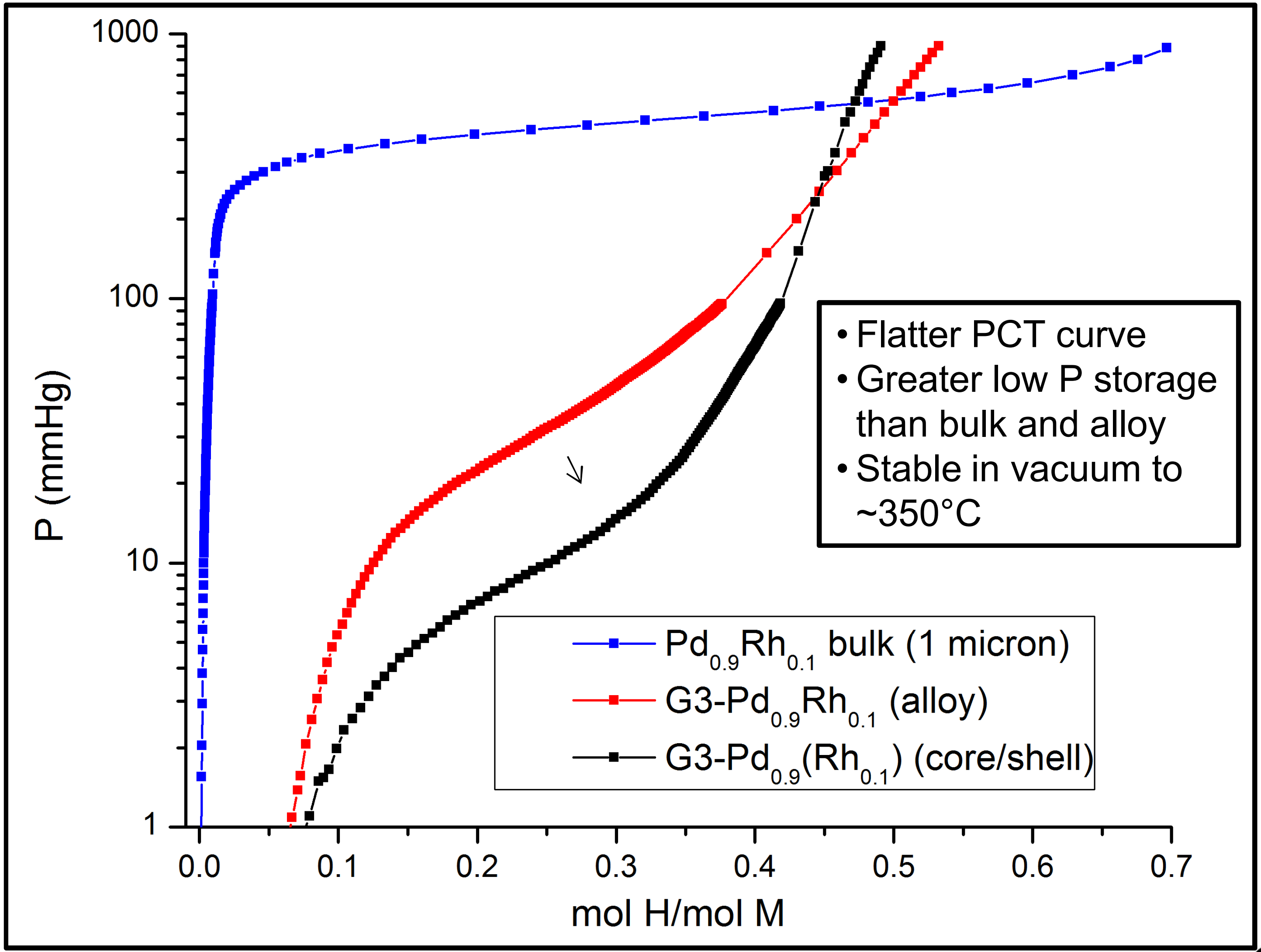
G3-$Pd_{0.9}(Rh)_{0.1}$ H_2 storage properties



Bulk $Pd_{0.9}Rh_{0.1}$ provided by N. Yang

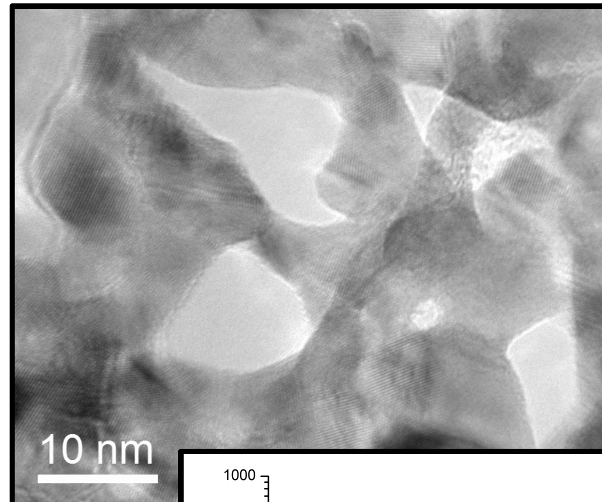
Summary and Outlook

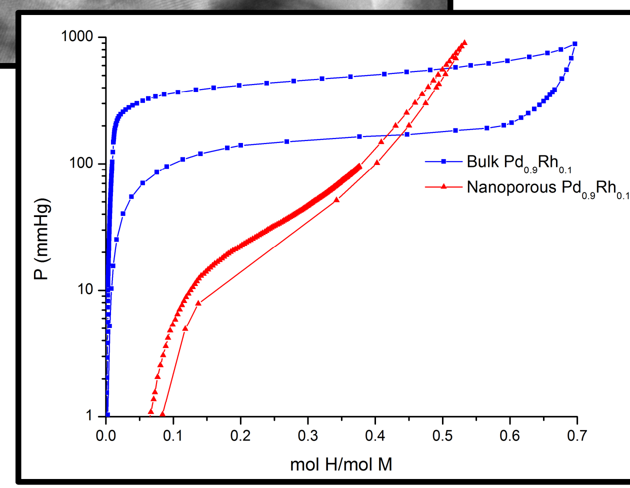
Highlights:

- New, unsupported, high surface area Pd alloys prepared for Hydrogen isotope storage
- Compositional uniformity leads to uniformly stable pore structure (~400°C)
- H_2 storage thermodynamics similar to previous reports for nanocrystalline/nanoporous Pd alloys
- Much faster kinetics of H-loading compared to bulk alloy
- Core/shell precursor leads to flatter, more Pd-like H_2 storage

Future Work:

- Spectral imaging of alloy and core/shell material
- More detailed kinetics (isotope exchange)
- ^{3}He implantation, evolution
- Hierarchical Pores





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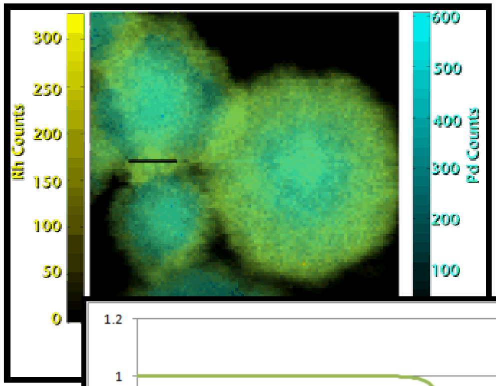

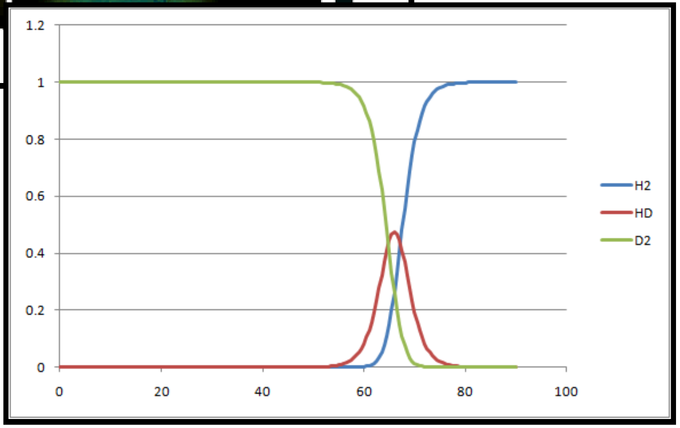

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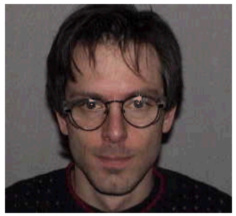
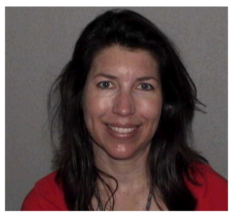
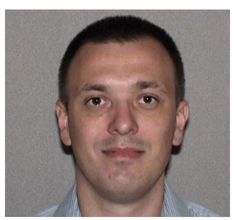


David Robinson

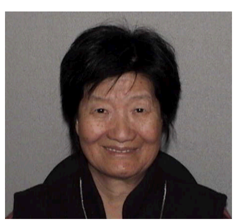


Michelle Hekmaty

Benjamin Jacobs, Protochips, Inc.



Vitalie Stavila



Nancy Yang

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