SAND 2013-3296C

Sandia National Laboratories

# Nanoporous Metals for Prevention of Helium Bubble Formation in Pd Tritides

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Sandia National Laboratories
Livermore, CA and Albuquerque, NM

Tritium Focus Group meeting
April 2013

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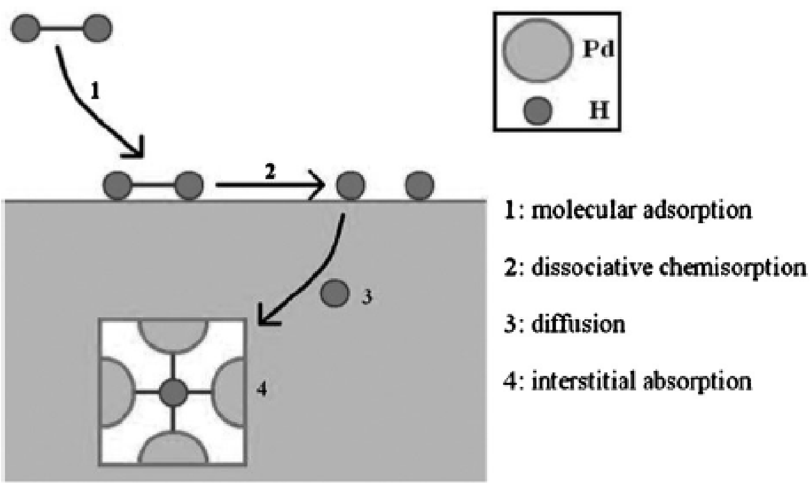
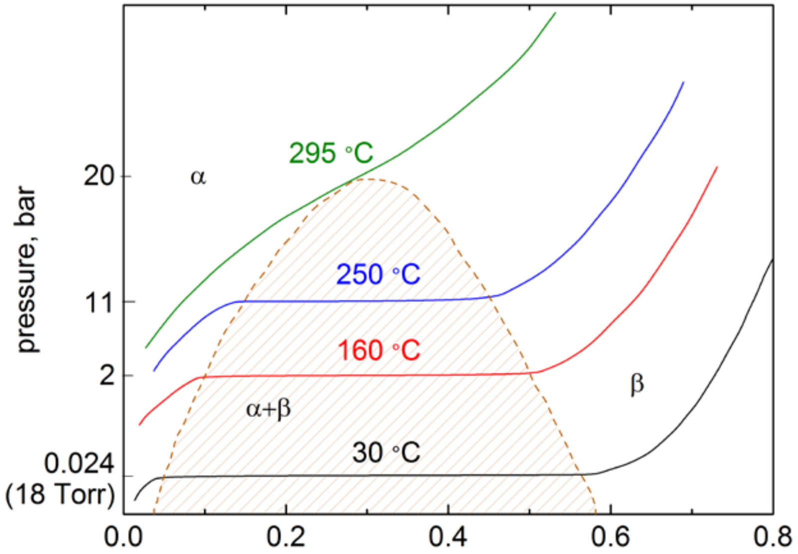
# Pd-H System

- Most extensively researched M-H system (~150 y)
- High $H_2$ solubility & mobility in Pd lattice
- H occupies octahedral sites, accompanied by a lattice expansion
- ~0.6 mol H/mol Pd near room temperature at P ~ 10 mmHg
- Applications in $H_2$ storage, catalysis, electrochemical, isotopic separations
- Useful for high-value applications including tritium storage which is an essential fusion technology

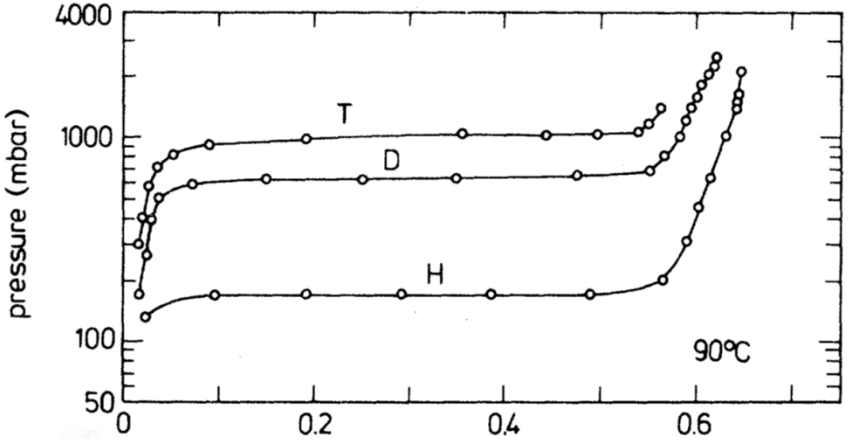



R. Delmelle, J., Phys. Chem. Chem. Phys. (2011) p.11412

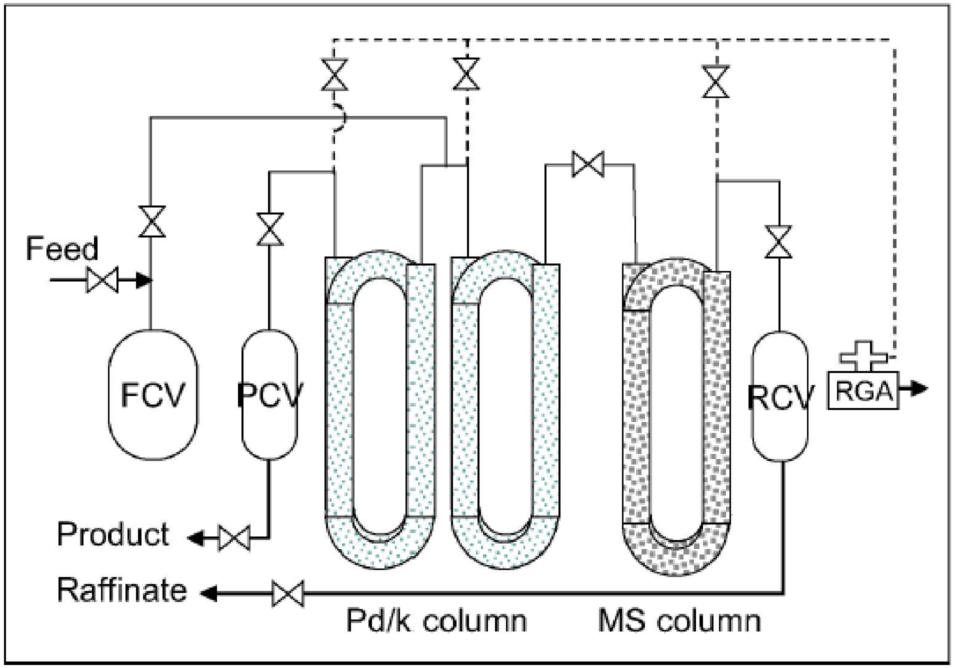



A.G. Knapton
Plat. Met. Revs 21:44 (1977)

# Isotope separation system



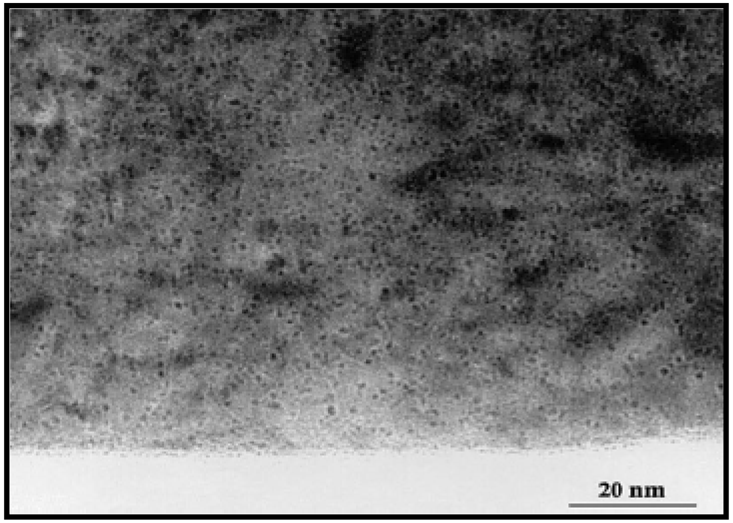

Strong isotope effect in Pd
R Laesser, Phys Rev B 26 3517




Savannah River isotope separator
- Flows gas mixture repeatedly over Pd
L. K. Heung *et al.*, Fusion Sci Tech 60 1331 (2011)

# Helium Bubbles Cause Problems During Long-term Tritium Storage in Pd:

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




TEM image shows defects from Pd-T aged 3 months

- $^{3}He$ in bulk metal nucleates to form bubbles that distort the metal lattice
- $^{3}He$ clusters expand and eventually force ejection of metal atoms from lattice sites
- Defects, changes in mechanical properties, changes in thermodynamics of hydrogen storage, uncontrolled $^{3}He$ release

Cowgill, D., Fusion Science and Technology, 28 (2005) p. 539
Trinkaus, H. *et al*., Journal of Nuclear Materials (2003) p. 229
Thiebaut, S. *et al*. Journal of Nuclear Materials (2000) p. 217

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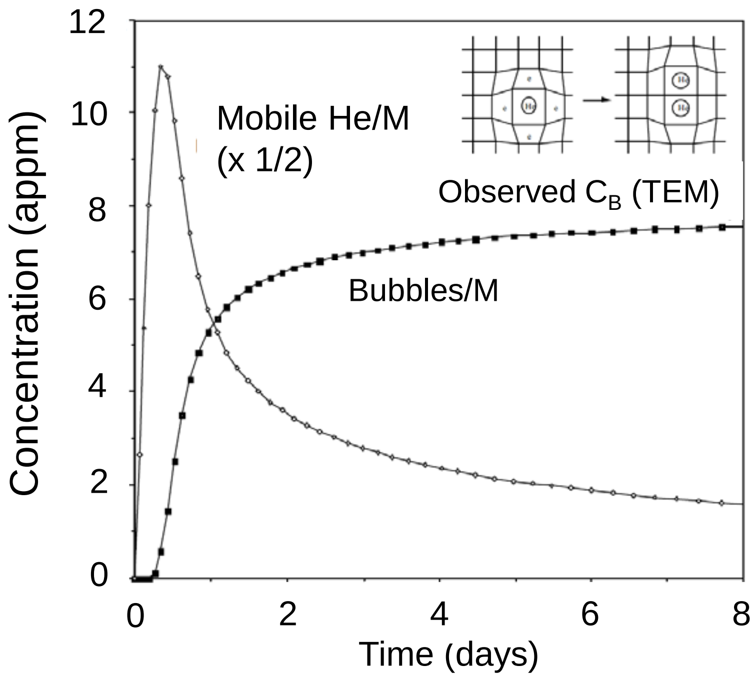


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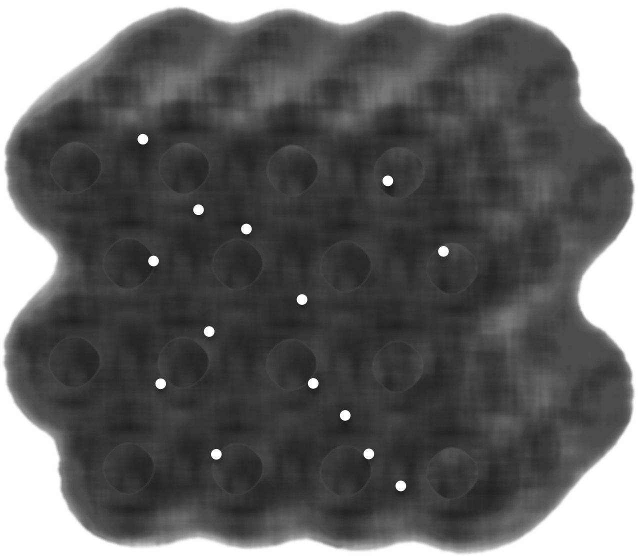
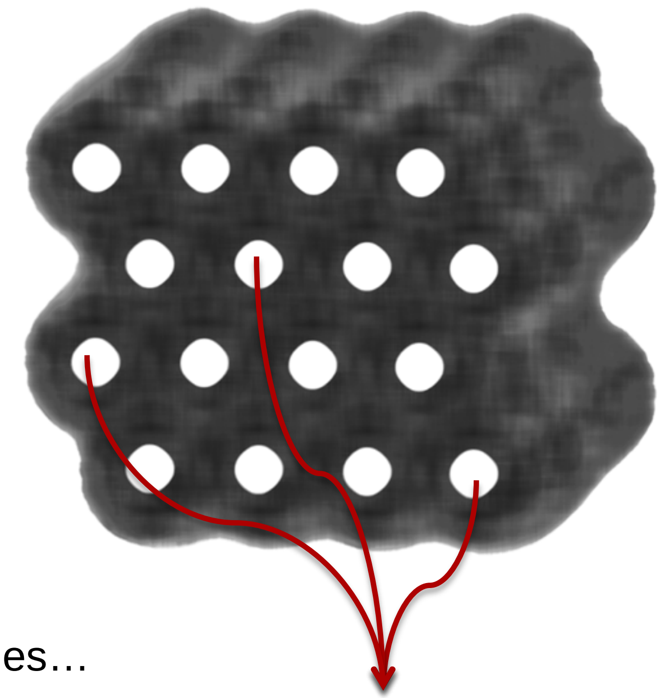
# Harmful Effects May Be Mitigated in Nanoporous Pd:

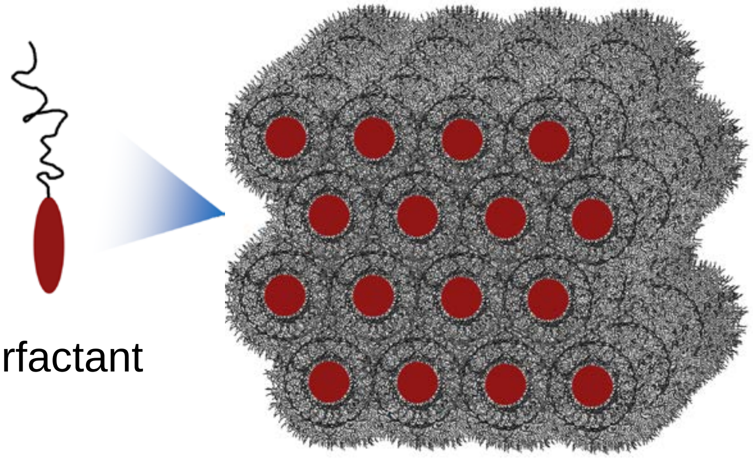




Instead of ejecting metal atoms, causing vacancies…

Helium atoms forming near pores should diffuse harmlessly away through channels…

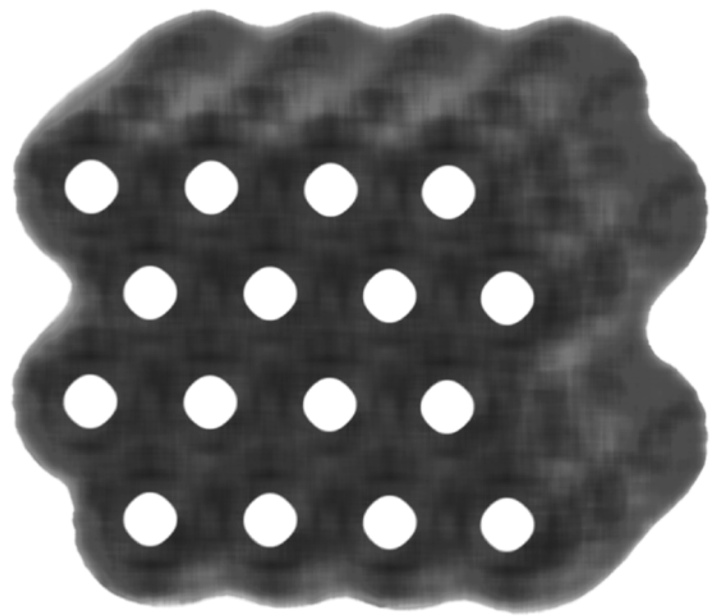
# Strategy: Chemical Reduction in Molecular Template



surfactant

self-assembly into hexagonal array

1. Metal Salt Loaded into aqueous phase
2. Chemical Reductant
3. Wash



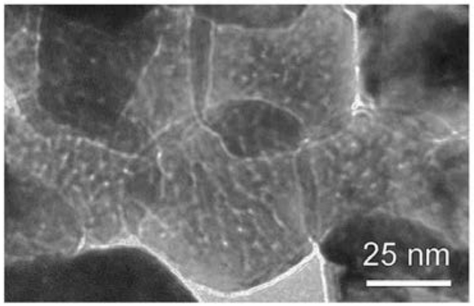
yields nanoporous metal

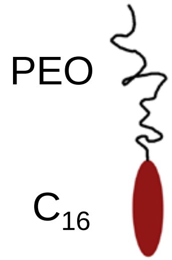
- Adapted synthetic methods:
  - Large quantities
  - Powders
  - Several pore sizes
- Metal salts are reduced around hydrophobic cores
- Removal of template leaves nanoporous metal

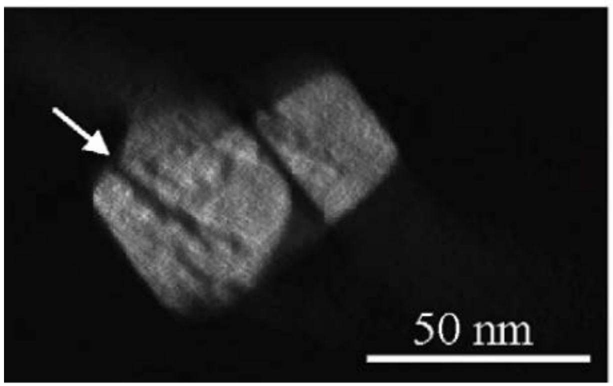
Kuroda, K. *et al.,* Angew. Chem. Int. Ed. 47 (2008) p. 5371
Attard *et al*., Science, 278 (1997) p. 838

# Three pore sizes from 3 to 13 nm

## “Brij-56” + $Pd^{2+}$ + 1% $H_2/N_2$

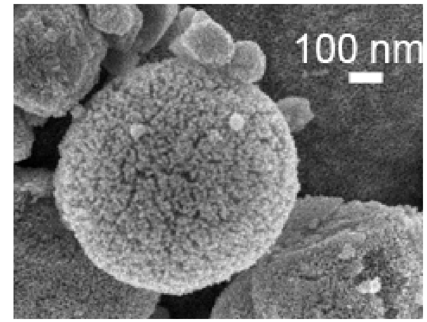


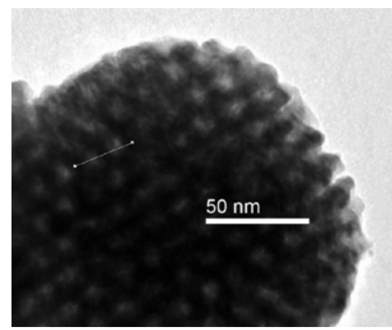




3 nm pores
Template MW ~ 600 g/mol

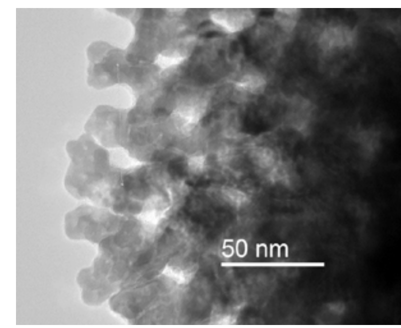
## PS-*b*-PEO block copolymer + $Pd^{2+}$ + 1% $H_2/N_2$








7 nm pores
Template MW ~5400 g/mol




13 nm pores
Template MW ~8800 g/mol

Robinson, D.B. *et al.*, Int. J. Hydrogen Energy 34 (2009), p. 5585
Robinson, D.B. *et al.*, Int. J. Hydrogen Energy 35 (2010), p. 5423
Cappillino, P.J. *et al.*, J. Mater. Chem. A 1 (2013) p 602

# Synthesis of Nanoporous Pd

## bcp/Pd$^{II}$ mixture

- $(NH_4)_2(Pd^{II}Cl_4)$ in $H_2O$
- (bcp-2.3,3.1k) in THF
- Solutions mixed,  THF removed by evaporation

## reduced paste

- Resulting paste reduced over 48 hours in humidified 1% $H_2$ in $N_2$

## bcp-Pd

- Reduced paste dissolved in THF/$H_2O$
- Free-flowing powder after removal of bcp-2.3,3.1k with solvent wash

| | |
|---|---|
| bcp-2.3,3.1k = polystyrene(2300)-*b*-polyethylene oxide(3100) | bcp-3.8,5k = polystyrene(3800)-*b*-polyethylene oxide(5000) |

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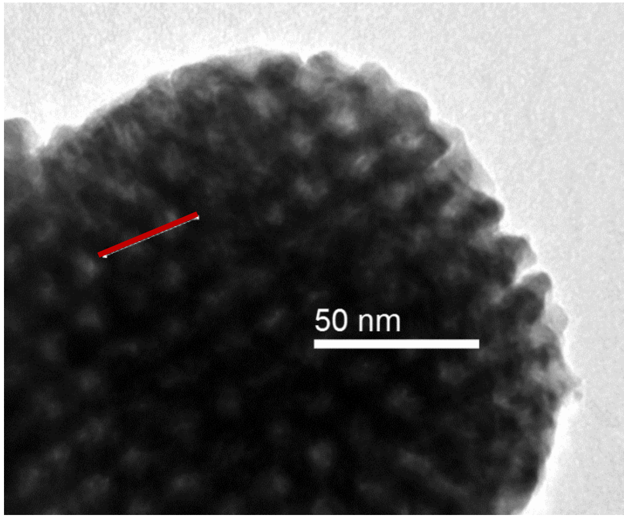
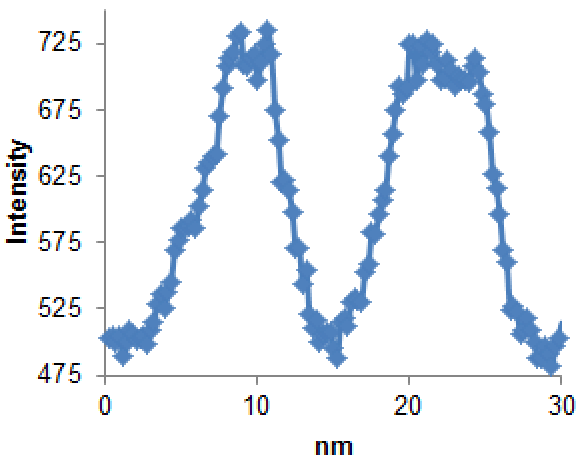
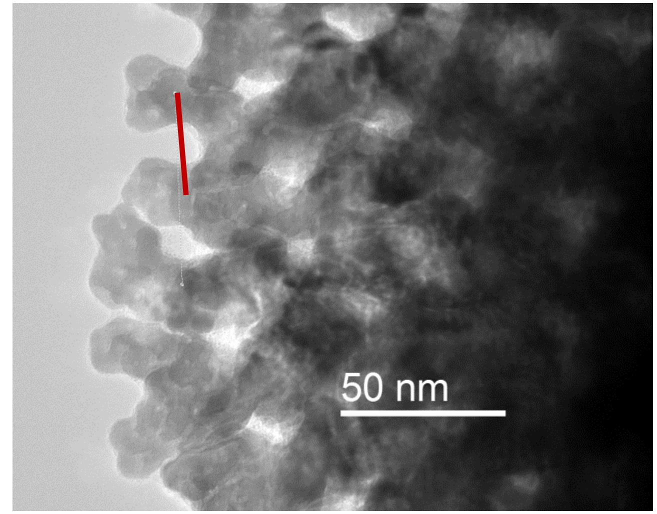
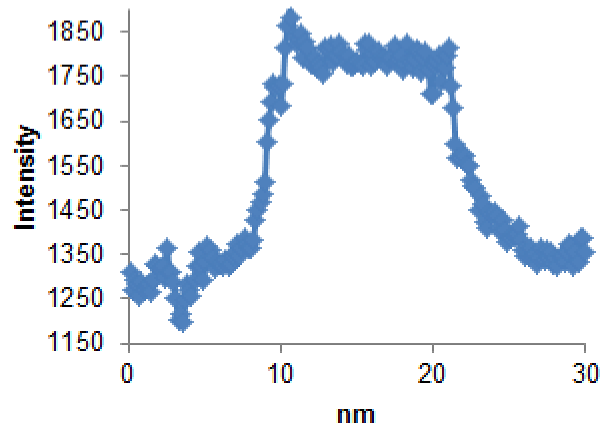
# Pore Size Tunable Based on Block Size



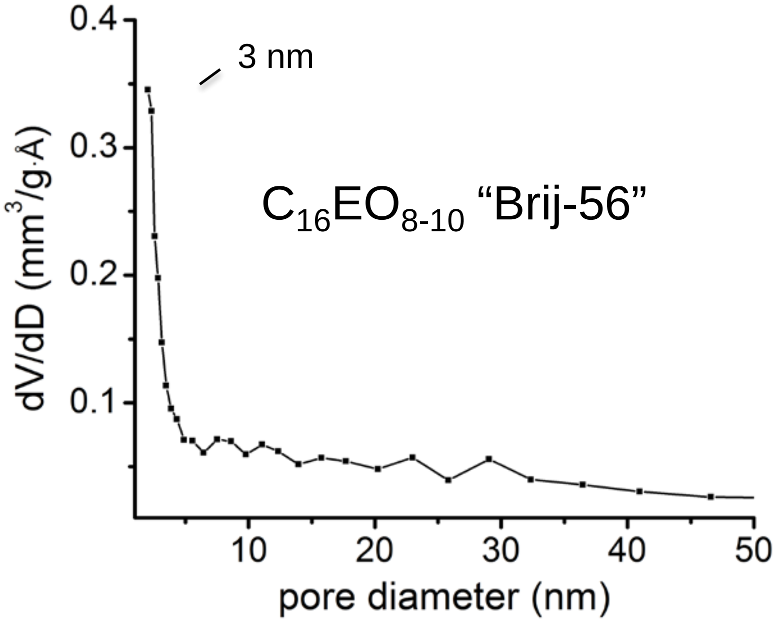

bcp(2.3,3.1k)-Pd
15 nm pitch, 7 nm pore

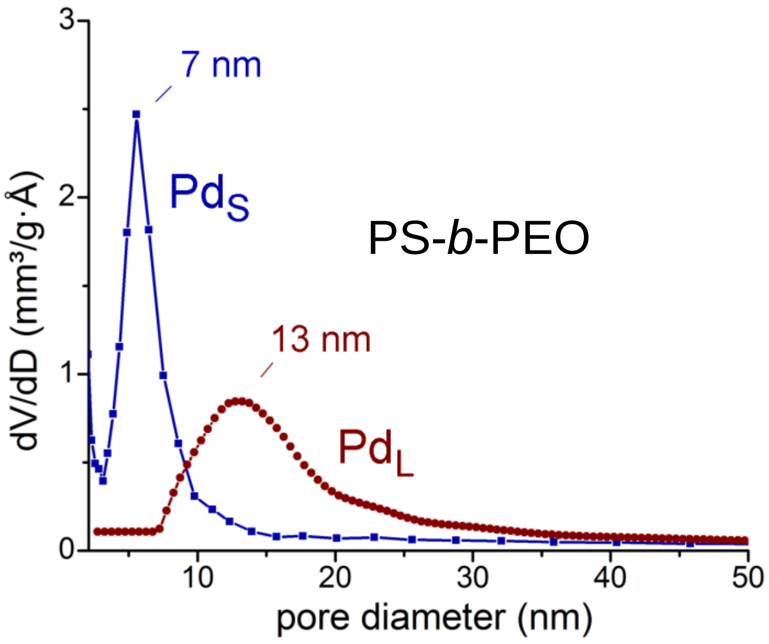



bcp(3.8,5.0k)-Pd
30 nm pitch, 12 nm pore

# Bulk Measurements Corroborate Microscopy




- Pore sizes of 3, 7, and 13 nm obtained with nitrogen porosimetry (BJH)
- Surface areas of 12, 6.4 and 8.1 $m^2$/g for $Pd_3$, $Pd_7$ and $Pd_{13}$, resp.

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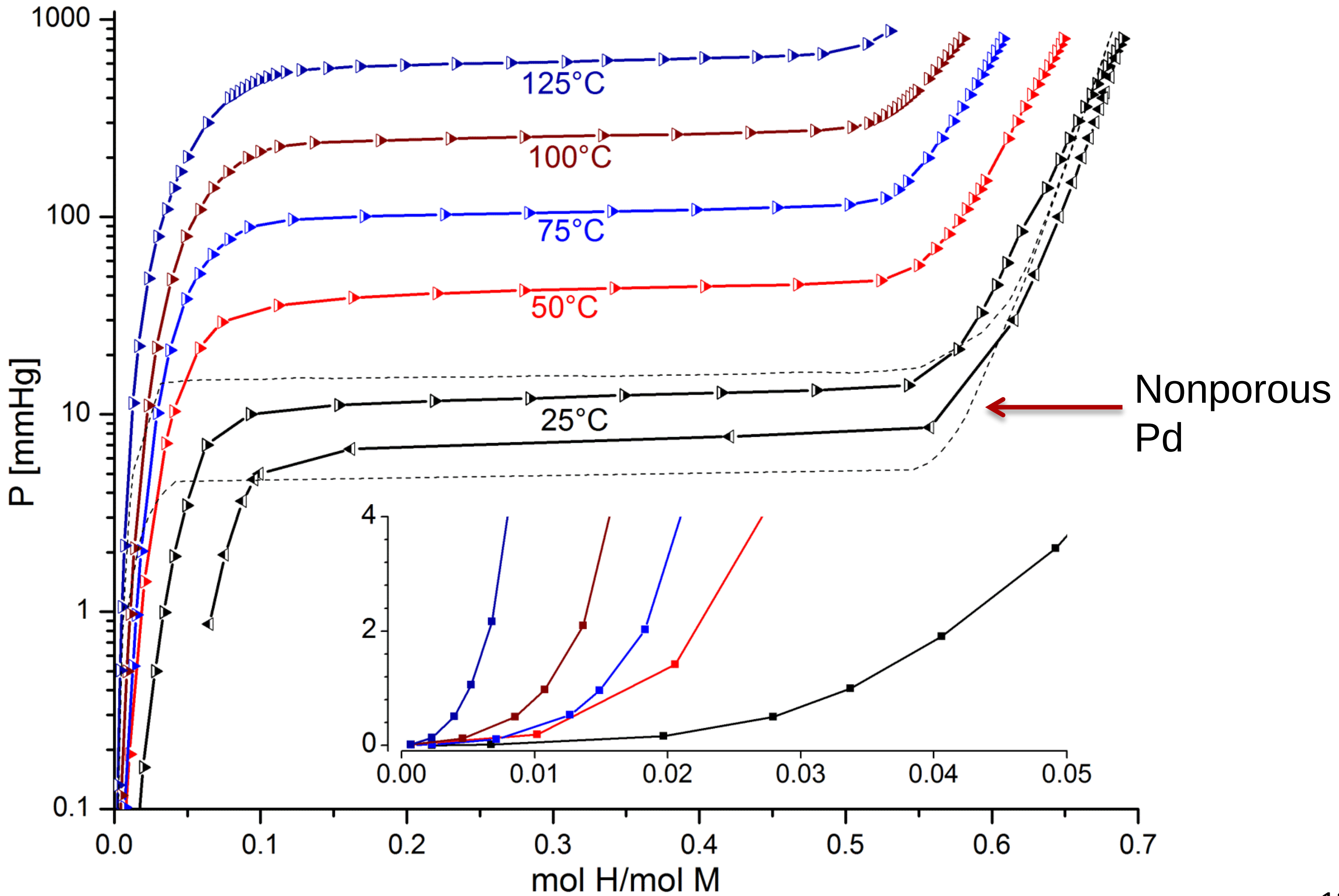
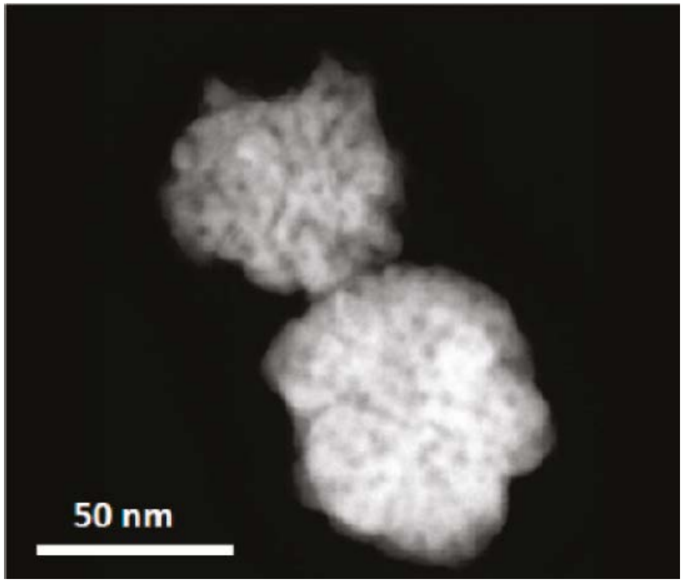
# $H_2$ Storage Properties similar to Nonporous Pd (3.8,5k shown here)

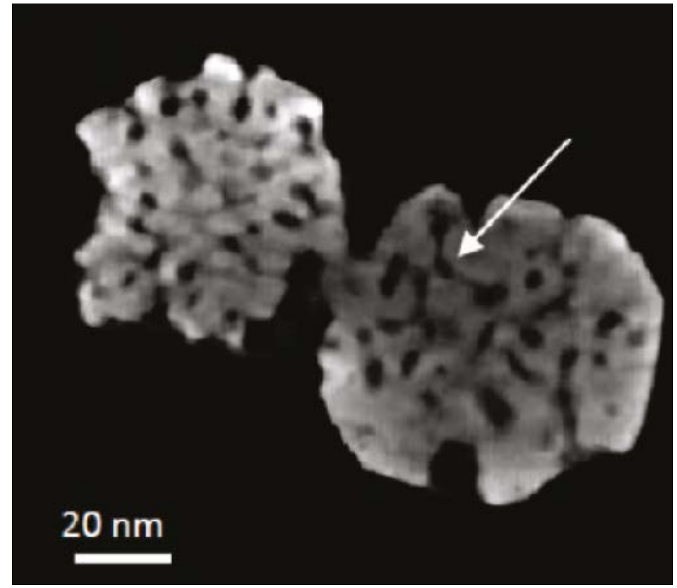


# Small Pores Collapse Between 300 and 600 C

"Brij-56"
3 nm
pores




Room Temperature

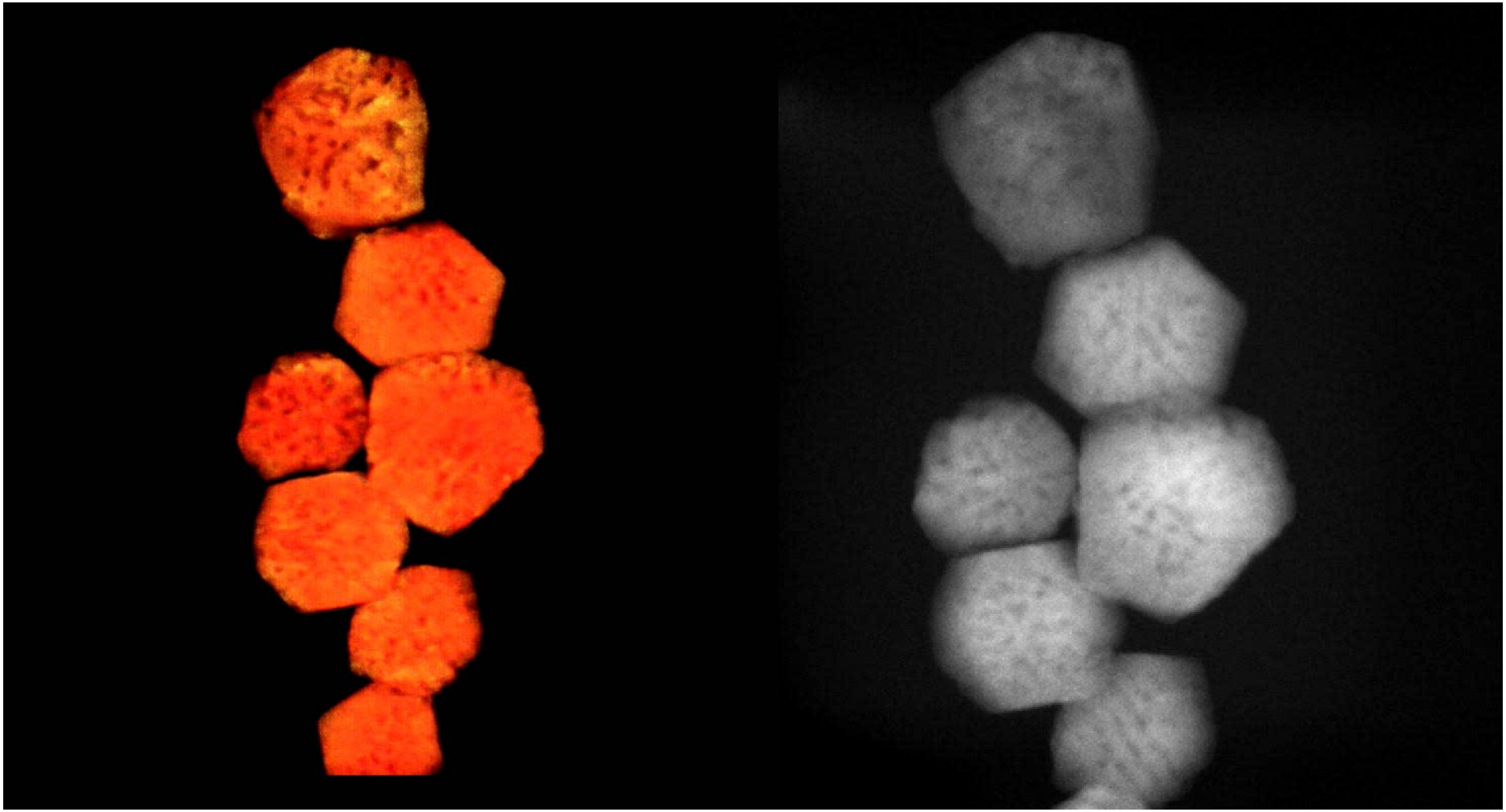



600°C

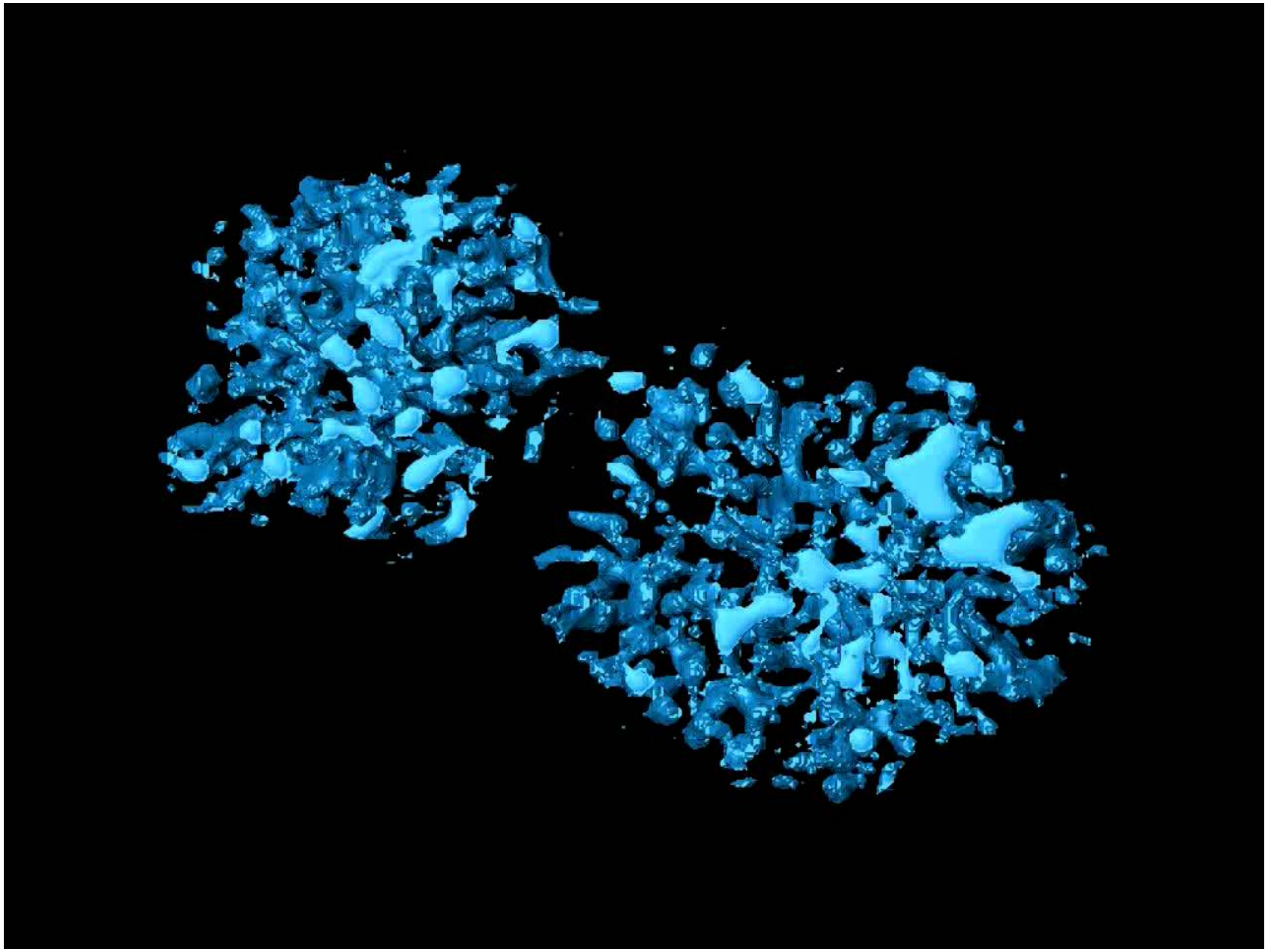
- STEM and STEM-tomography show that pores begin to collapse near 300°C
- By 600°C Pores have coalesced into large voids

Klein, *et al.*, J. Am. Chem. Soc. 2011, 133, 9144–9147

# Electron tomography

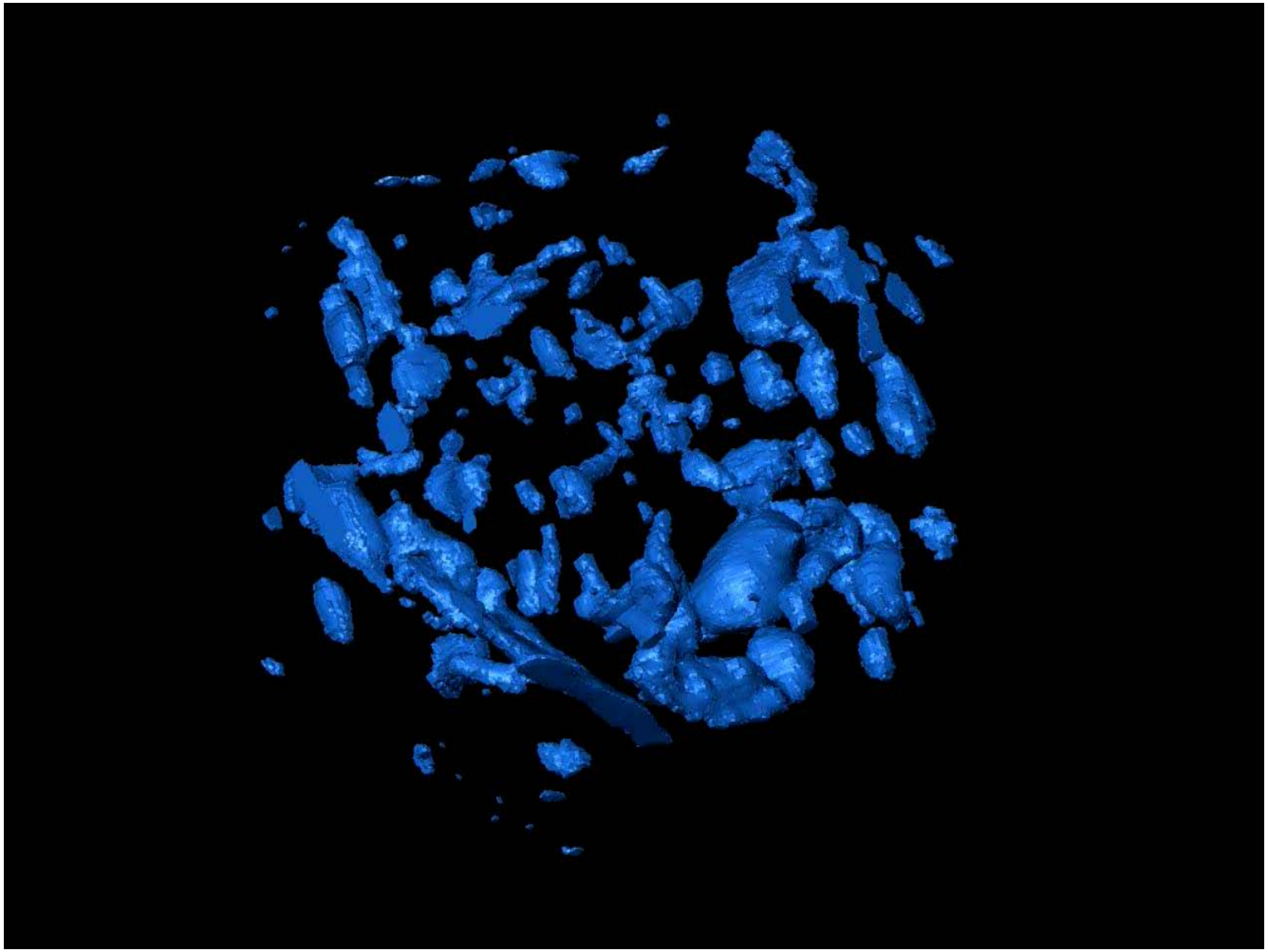


# Pore tomography – 25 C



Klein, *et al.*, J. Am. Chem. Soc. 2011, 133, 9144–9147

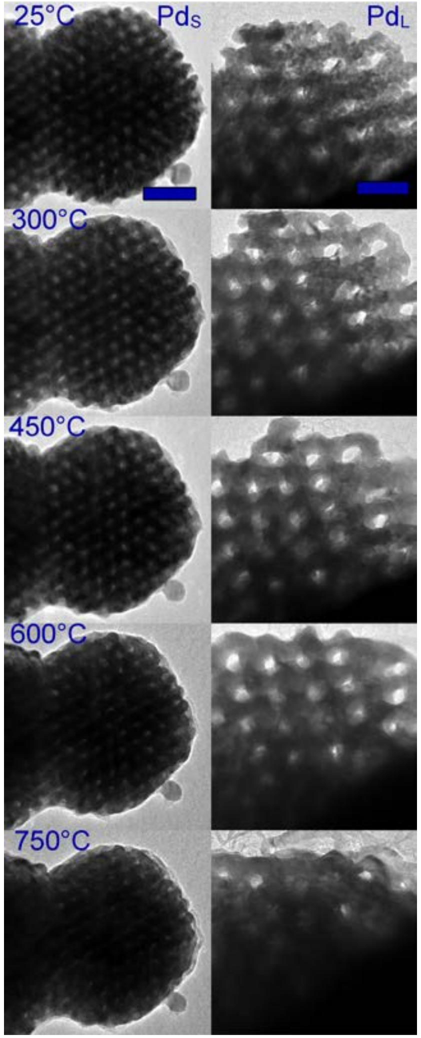
# Pore tomography – 600 C

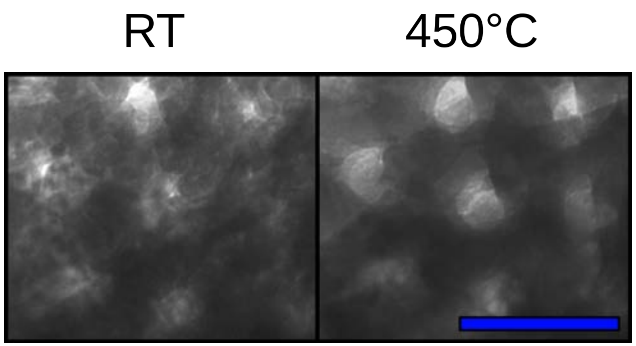


Klein, *et al.*, J. Am. Chem. Soc. 2011, 133, 9144–9147

# 7 & 13 nm pores stable to > 600 C

Both 7 nm (left) and 13 nm (right) pores are intact to 600°C. Collapse occurs by 700°C




NP forming ligaments fuse upon annealing (small voids collapse)

Pore structure remains

50 nm scalebars

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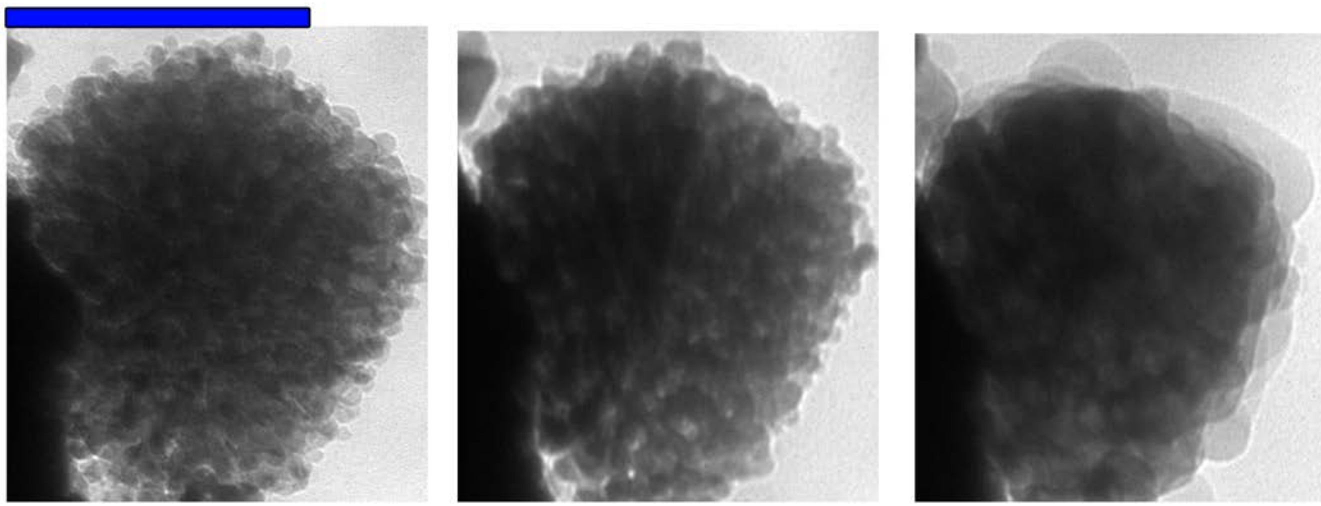
# *In situ*, gas cell investigations:

TEM images at 125°, under 1 atm $H_2$ after several pulses to specified temperature




125°C 200°C 300°C

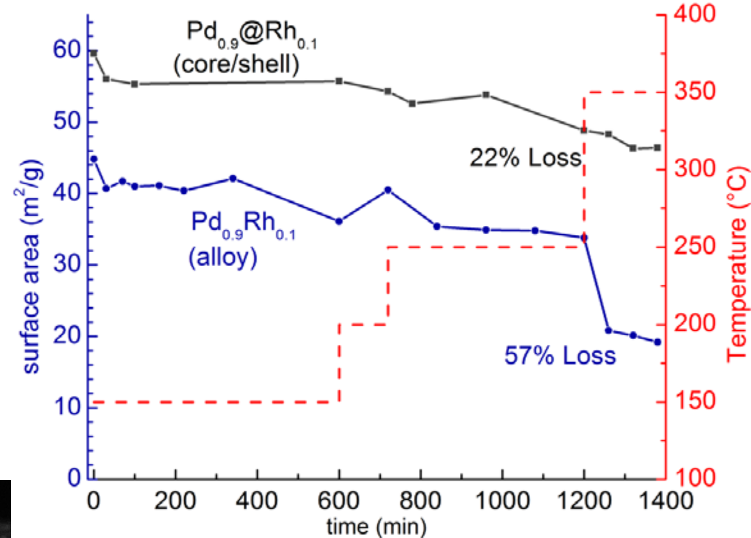
Possible factors contributing to decreased stability:

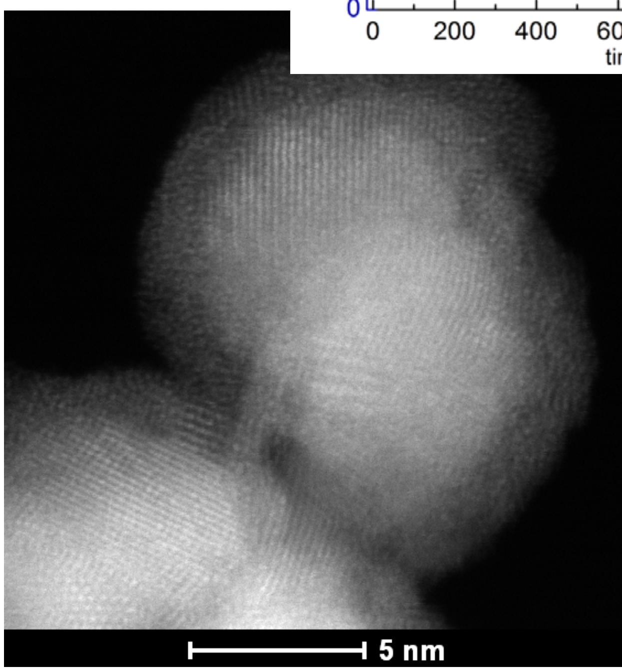
- Contraction from dehydriding
- Surface state

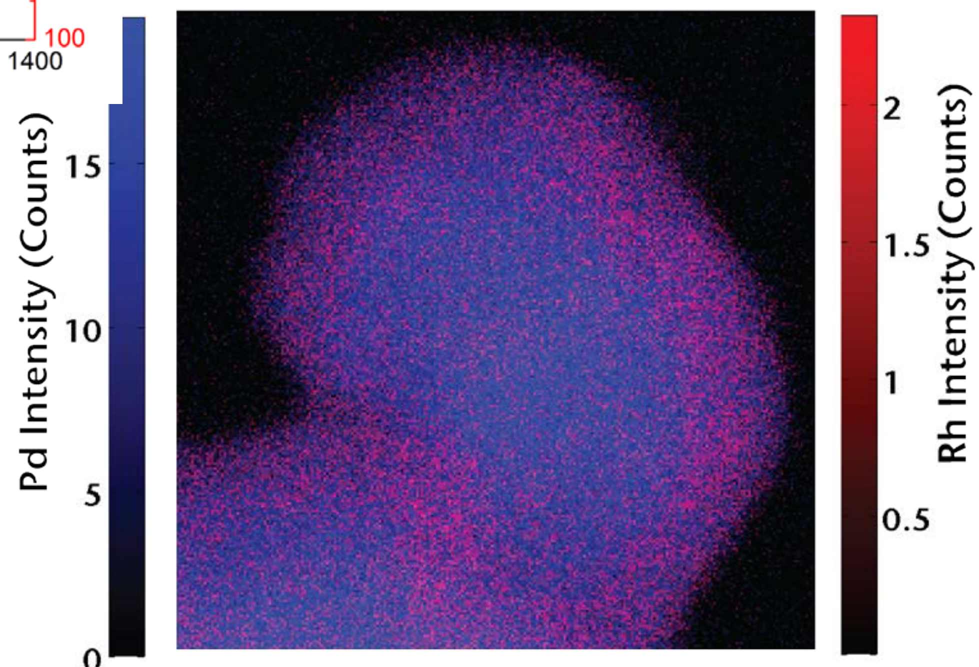
Cappillino, P.J. *et al.*, J. Mater. Chem. A 1 (2013) p 602

# Rh shell on Pd improves thermal stability

Cappillino, P.J. *et al.*,
J. Mater. Chem. 22 (2012) p 14103



# In situ heating

10-31-2010

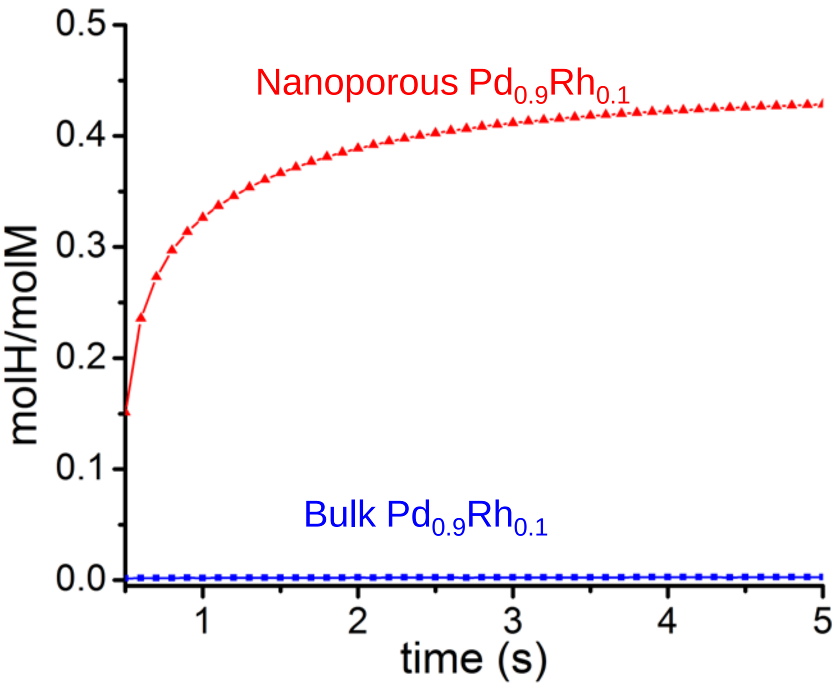
Pd:Rh 1:1

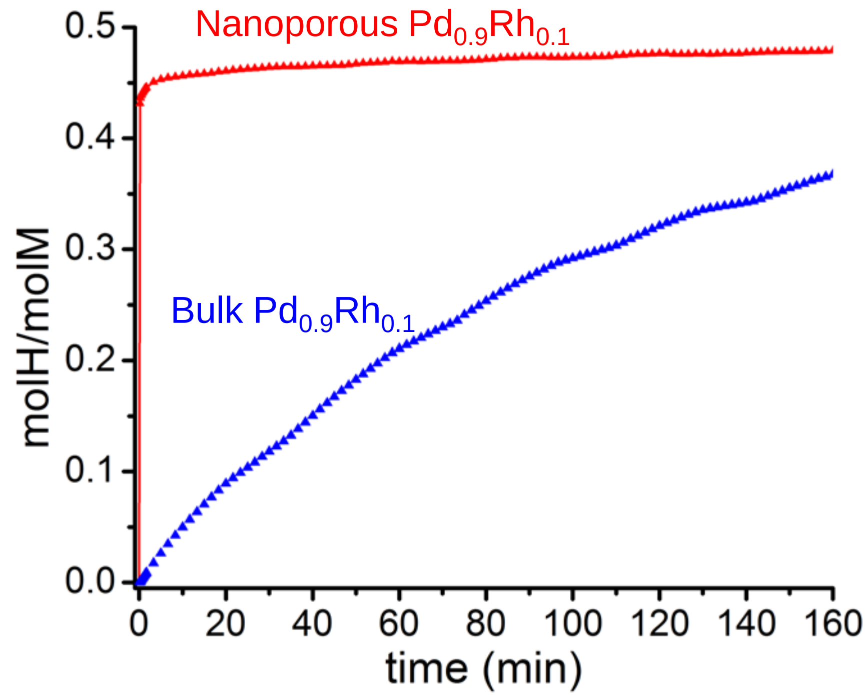
200 to 500 C

ML II 81-1

# $10^4$ X Faster $H_2$ Loading

650 Torr $H_2$ loading

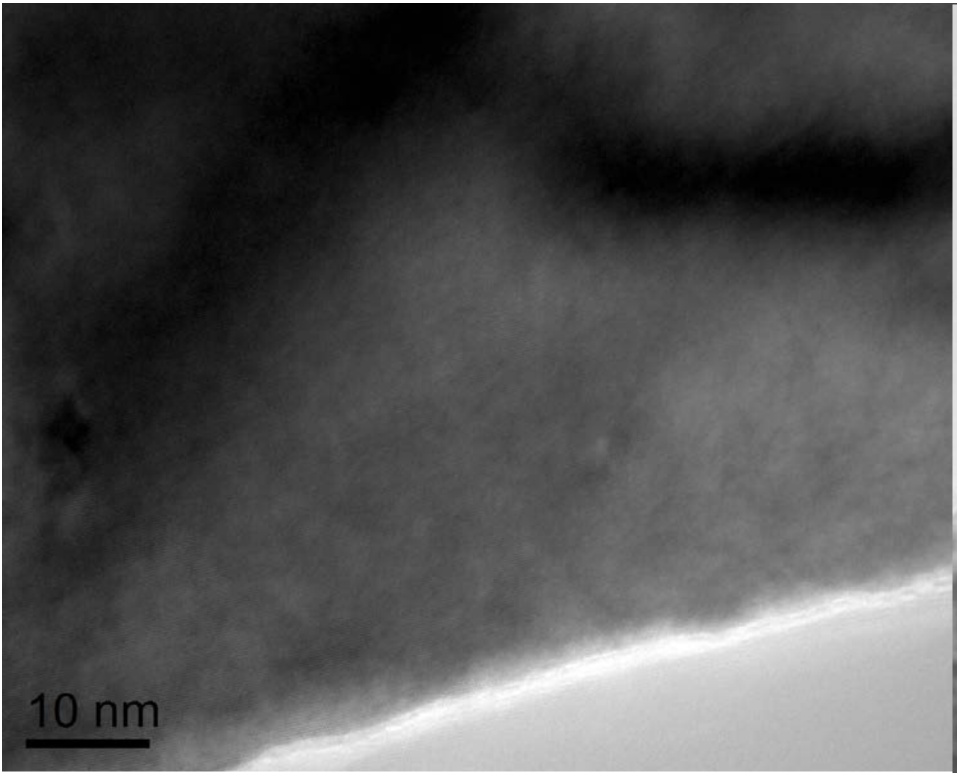


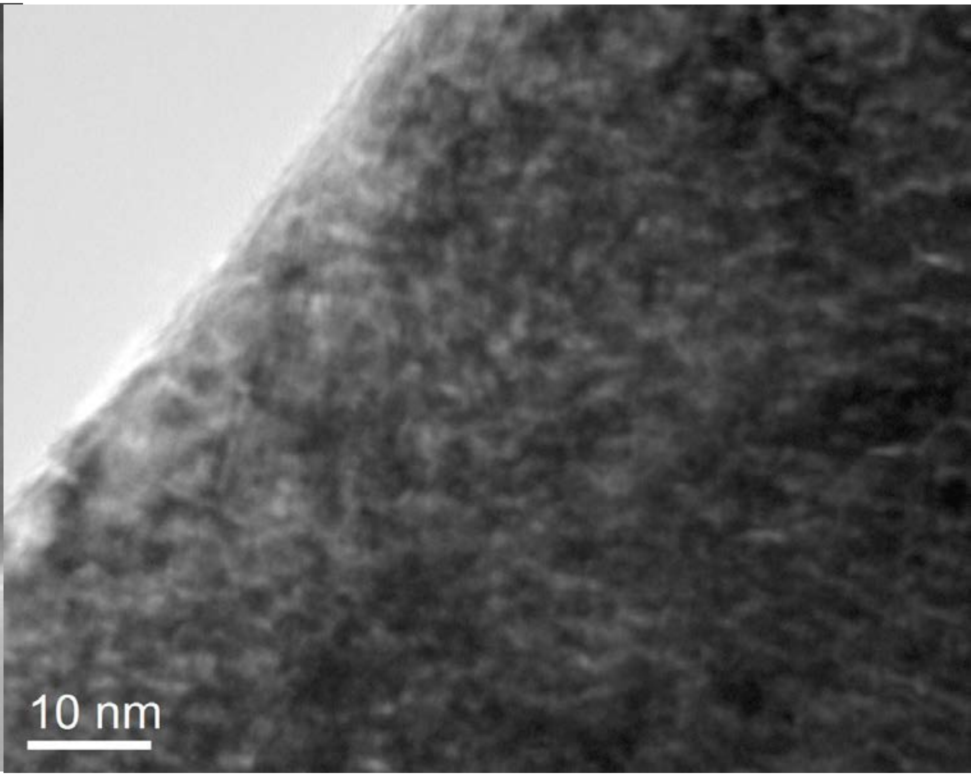

Cappillino, P.J. *et al.*,
J. Mater. Chem. 22 (2012) p 14103

Nonporous $Pd_{0.9}Rh_{0.1}$ provided by Nancy Yang

# Helium ion implantation in electropolished Pd foil



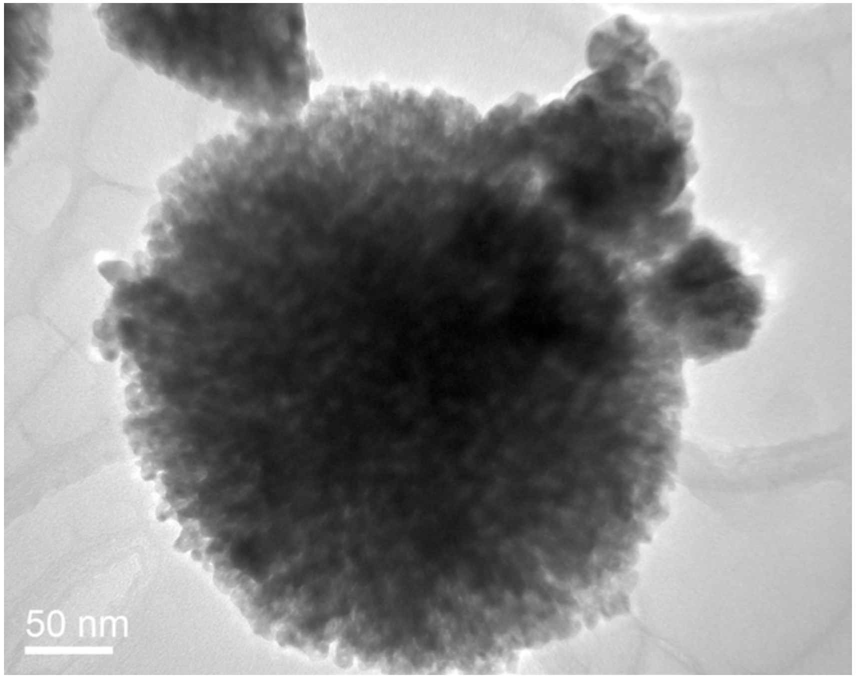

Before He



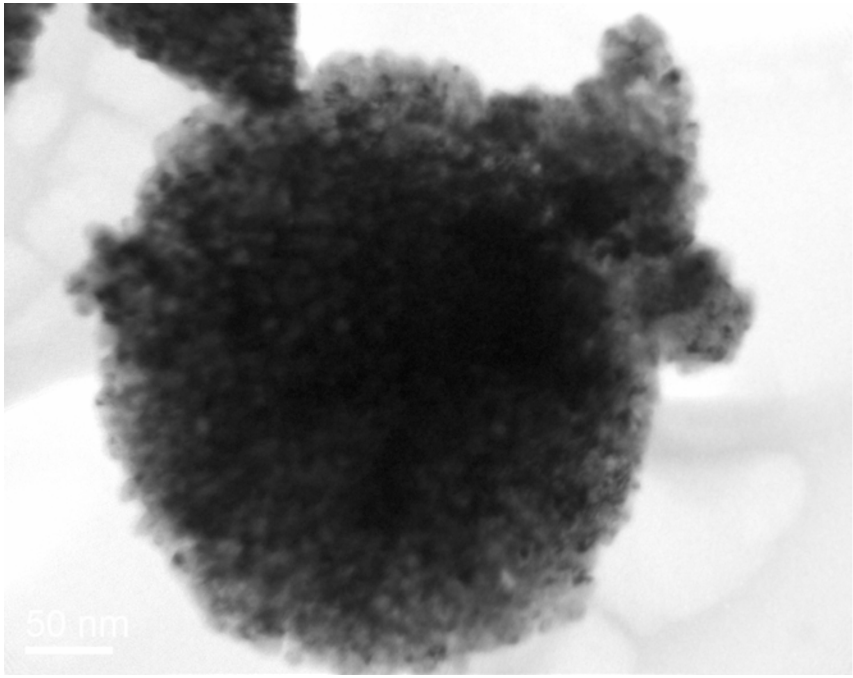

After He

He ion implantation is a relatively convenient but imperfect approximation of bubbles formed by $^3H$ decay.
Electropolishing a thick foil can create a hole with a sharp edge that has an electron-transparent region.
Argon ion milling, another sample prep method, creates its own bubbles in Pd foils.
5 keV He ions

# Less drastic changes are seen in nanoporous Pd



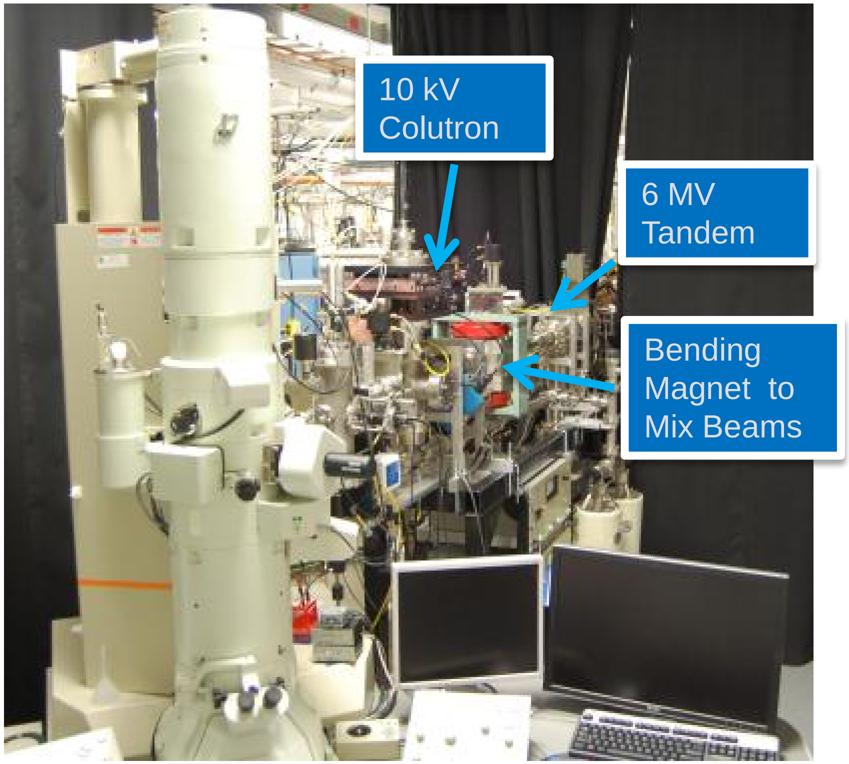

Before He




After He

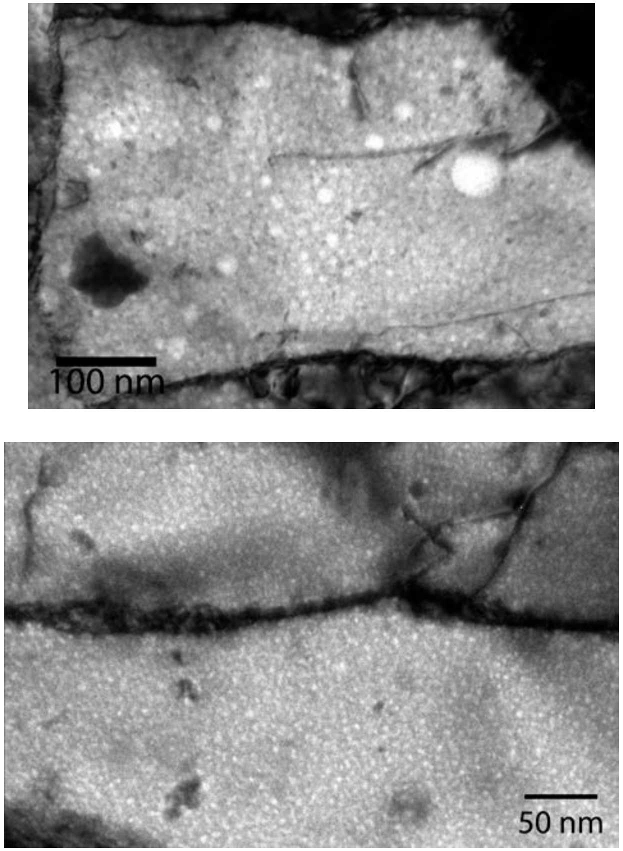
No obvious bubbles that are distinguishable from pores
Some loss of surface area, likely due to absorbed beam energy

# New capability: In situ TEM of He implantation




$I^3$TEM is providing insight into:

1) Loop formation
2) Loop stability & migration
3) He bubble formation & distribution
4) Rad & structural defect interactions




$I^3$TEM He implantation of SPD-W developed for ITER applications

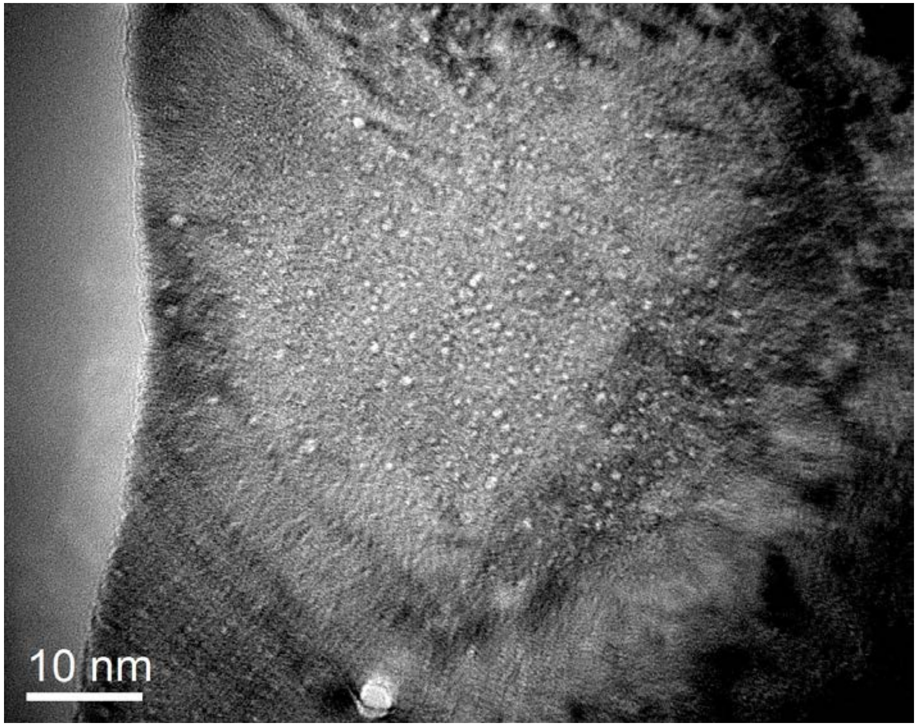


K. M. Hattar, O. El-Atwani, D. Buller, & J.A. Scott

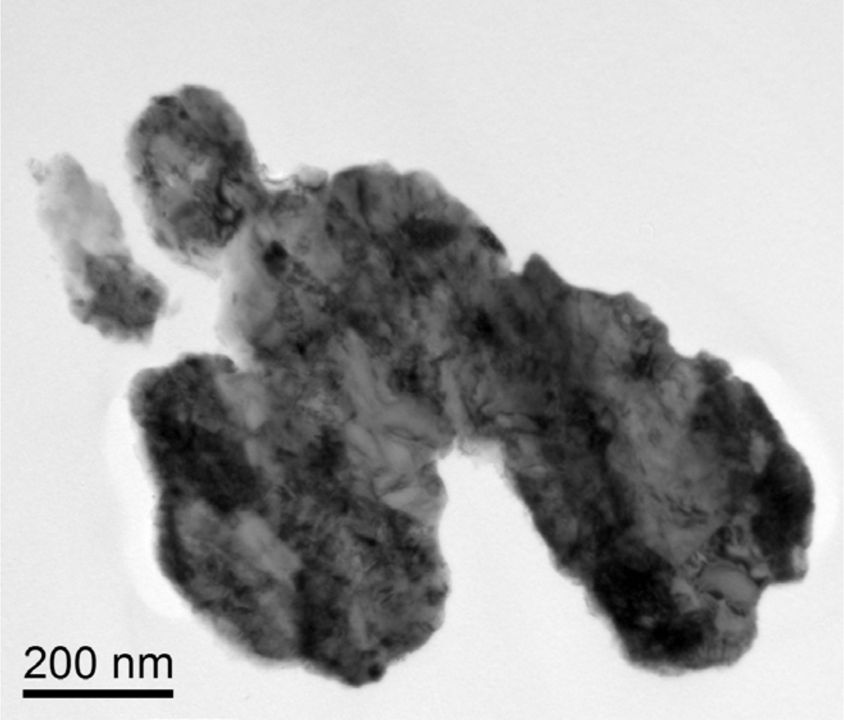
# TEM sample prep methods

Electropolishing generates aerosols and liter scales of perchloric+acetic acid waste

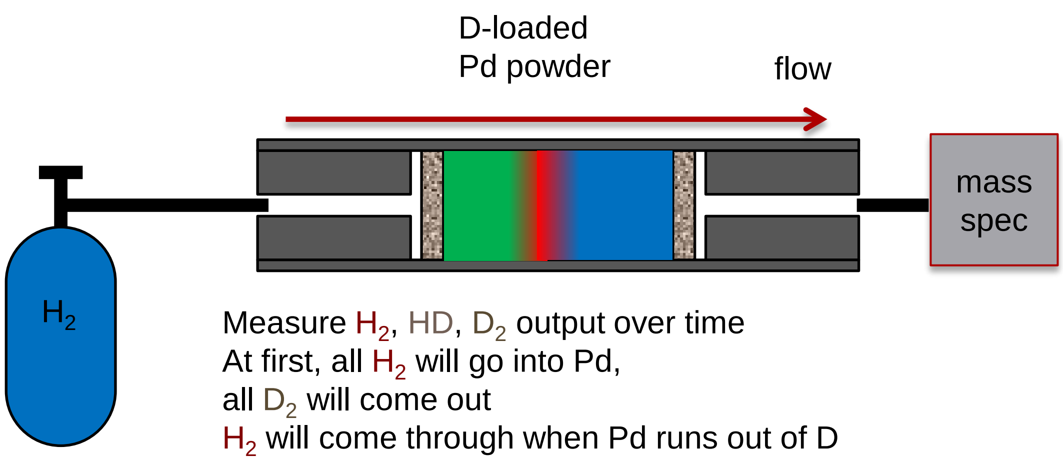
Ar ion milling introduces its own bubbles (no He implantation here)




Microtome creates electron-transparent samples with uniform thickness, minimal waste

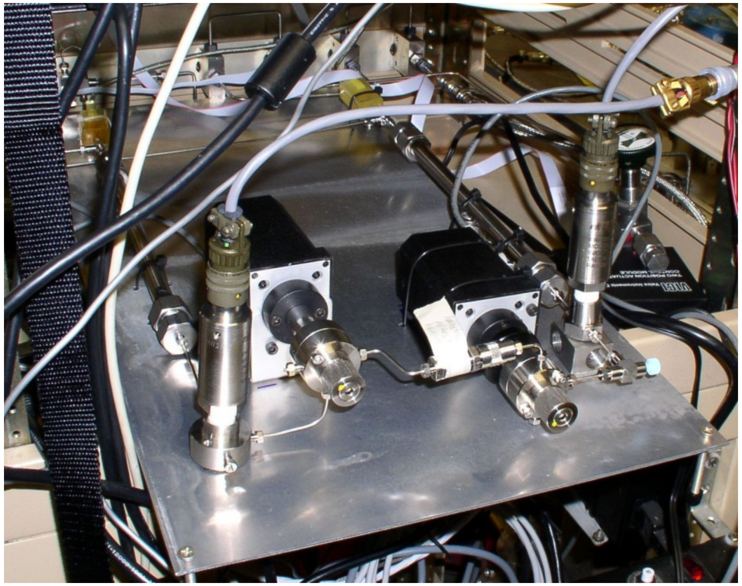


# Isotope transport kinetics experiments



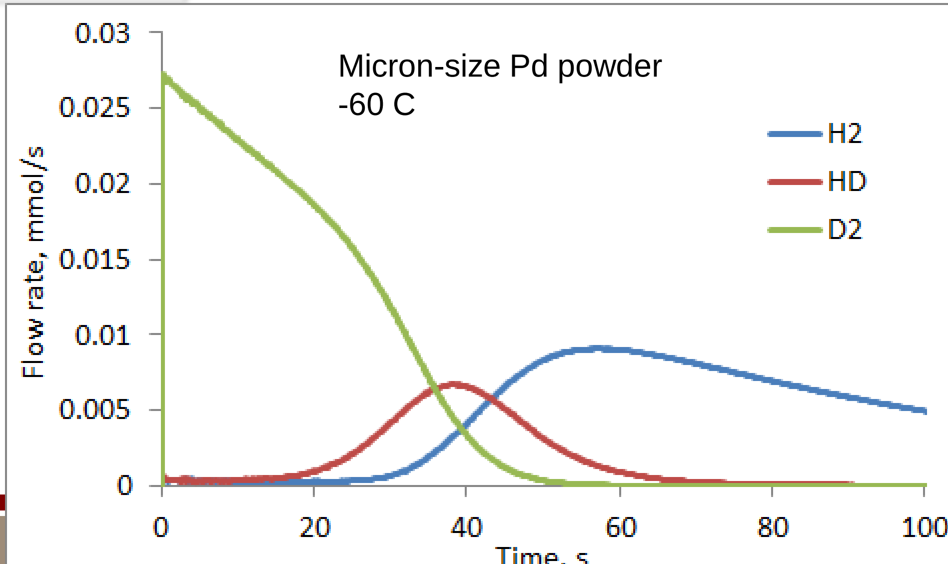

Measure $H_2$, HD, $D_2$ output over time
At first, all $H_2$ will go into Pd,
all $D_2$ will come out
$H_2$ will come through when Pd runs out of D

HD peak moves more slowly than overall gas flow




G.W. Foltz and C.F. Melius, J. Catal. 108 409 (1987)

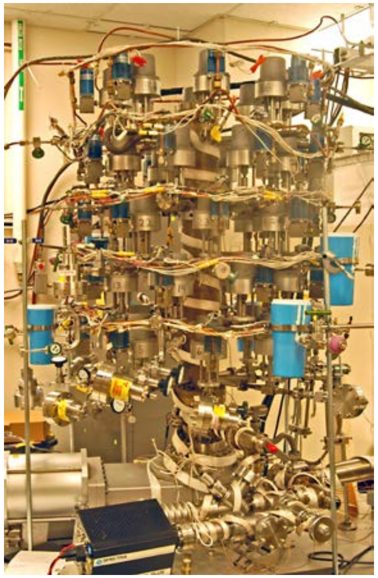
Nanoporous powders are flaky or oddly shaped
- Poor flow characteristics
- Tune in at MRS 2014



# Path to real tritium experiments

- Exceptionally small TEM sample size (pg to mg) yields a disproportionate amount of valuable scientific knowledge
- Preliminary data suggest that mg scale Pd-T samples can be easily cleaned to pCi range
- TEM operators routinely use pCi of uranyl contrast agents
- Dedicated sample prep and instrumentation at SNL/NM
- Other small-scale techniques: XRD, SEM of thin films

Tritium envelope facility with capture system

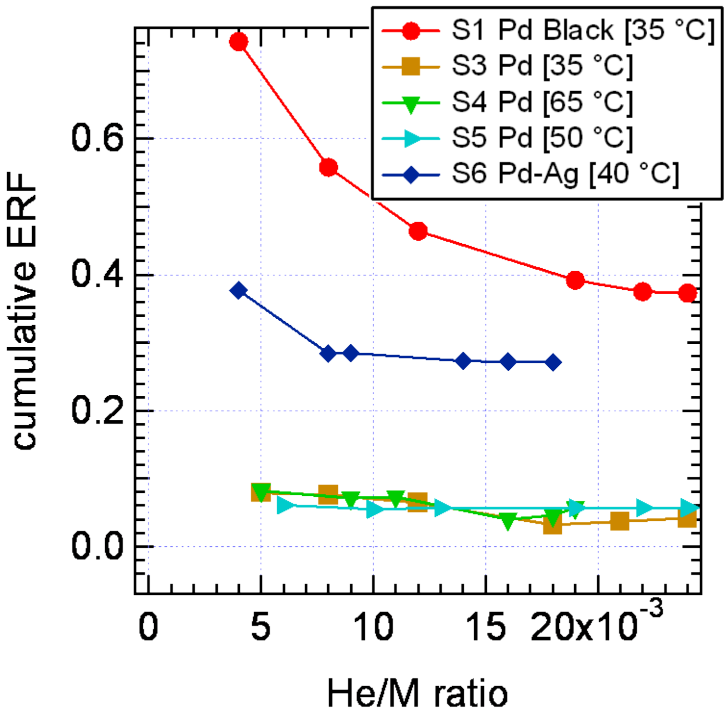


Sample exposure

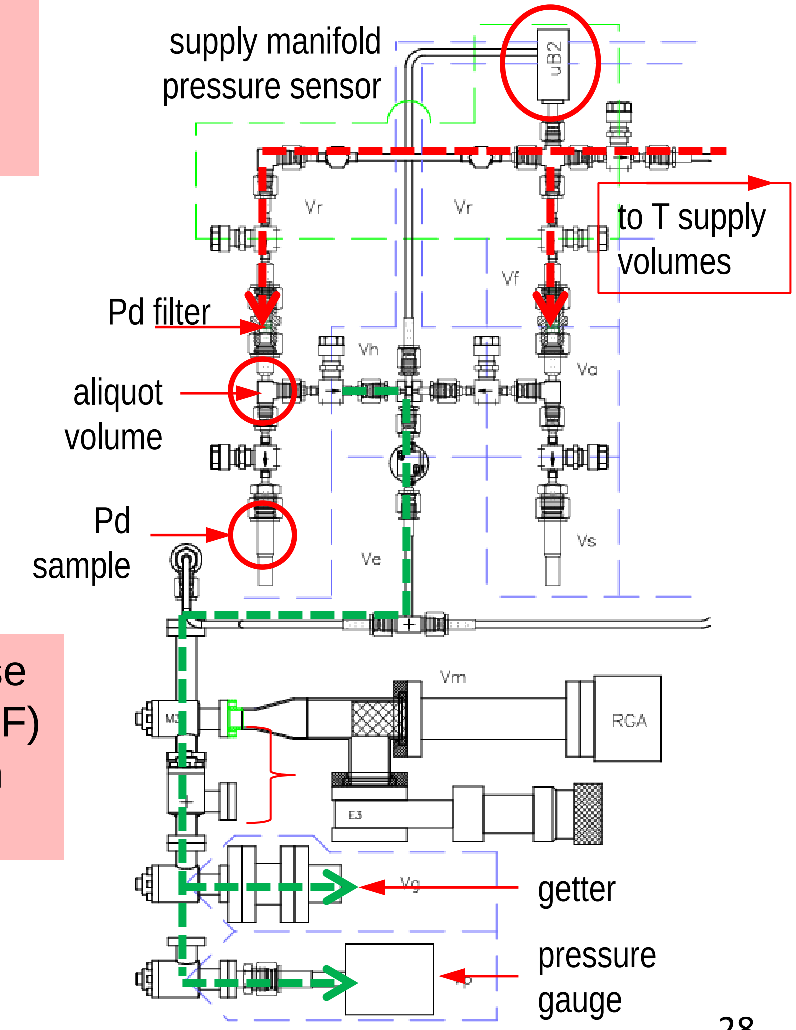
# Early $^3$He release experiments at LLNL

Sandia National Laboratories

- High surface area Pd retains much less He
- Measured from $^3$He pressure buildup in sample volumes
- Requires g-scale samples, but self-contained




Early Release Fraction (ERF) as a function of tritide age



# Summary

- Nanoporous Pd can be made in gram-scale batches
- Tunable pore size
- Apparently does not retain implanted He
- High surface area yields faster uptake/release kinetics
- Thermal stability may be an issue, but manageable by tuning pore size and composition
- Carefully working toward study of tritium-exposed samples

# Team


David Robinson
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drobins@sandia.gov


Pat Cappillino
Synthesis,
Bulk properties


Michelle Hekmaty
TEM/EDS


Josh Sugar
EDS imaging


Ilke Arslan
Pacific Northwest
National Lab
3D TEM


Rob Kolasinski
Early He release


Clark Snow
SNL/NM
Tritium facility


Khalid Hattar
In situ
Ion beam TEM


Don Cowgill
He bubble model


George Buffleben
Kinetics experiments