SAND2014-17018PE

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Synthesis and Thermal Stability Studies of Nanoporous Metals for Hydrogen Storage Applications by in situ TEM

Molecular Foundry User Meeting 2014

David B. Robinson

U.S. DEPARTMENT OF ENERGY
NNSA National Nuclear Security Administration

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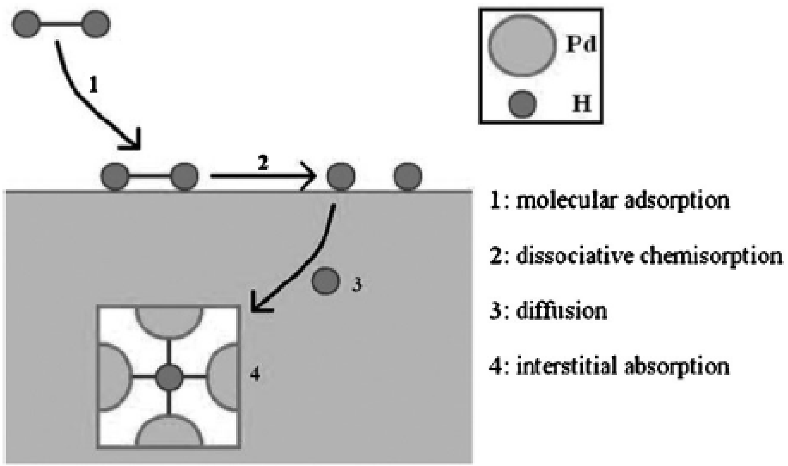
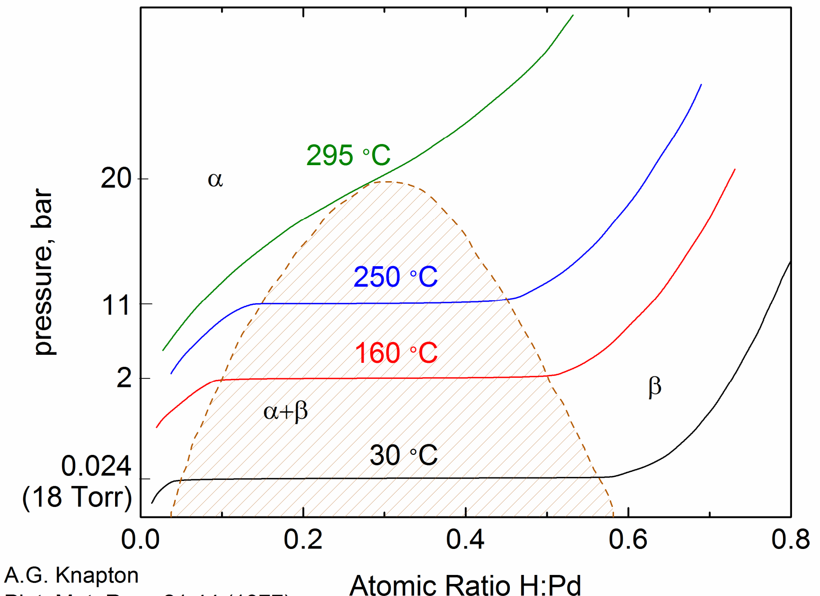
Palladium Hydride



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

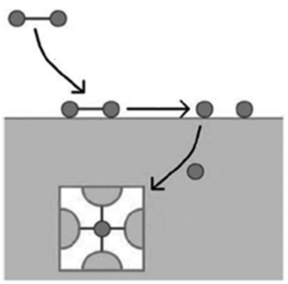


A.G. Knapton
Plat. Met. Revs 21:44 (1977)

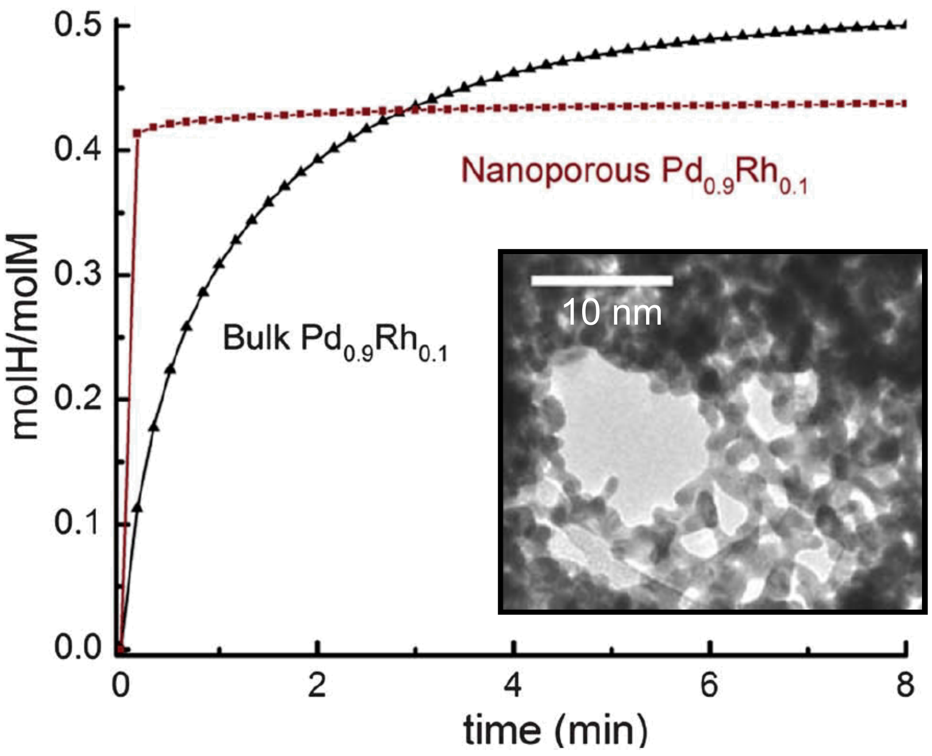
Near-stoichiometric amounts of H stored in octahedral holes
Lattice expansion above critical concentration (T,P dependent)
Other hydrides are of interest, including Pd alloys

Nanoporosity improves properties

1) higher surface area, smaller ligaments = improved kinetics



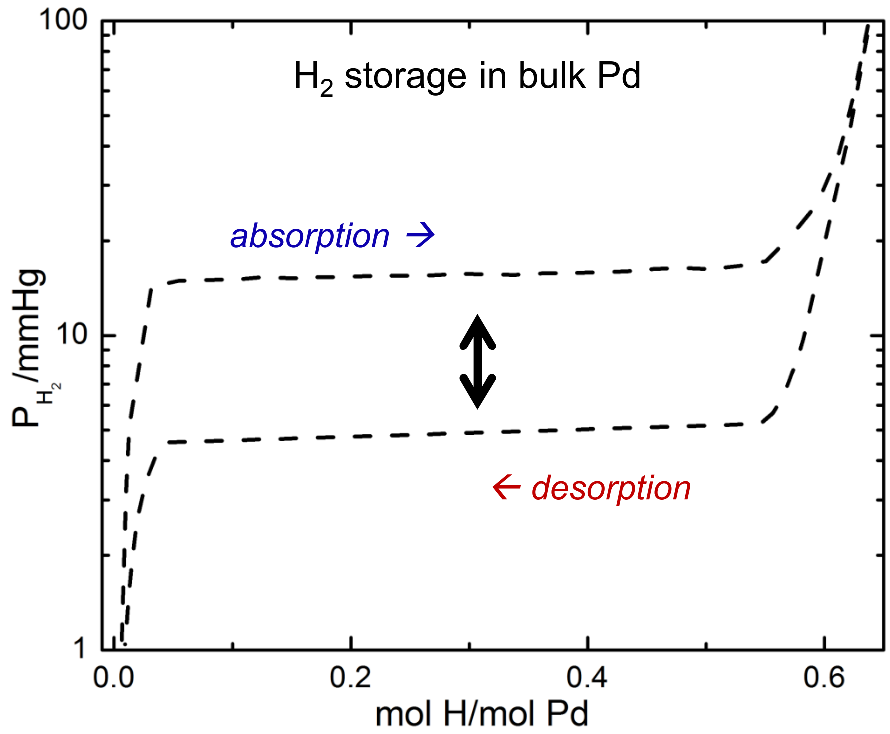
Cappillino *et al.*, J. Mater. Chem. (2012) p. 14013



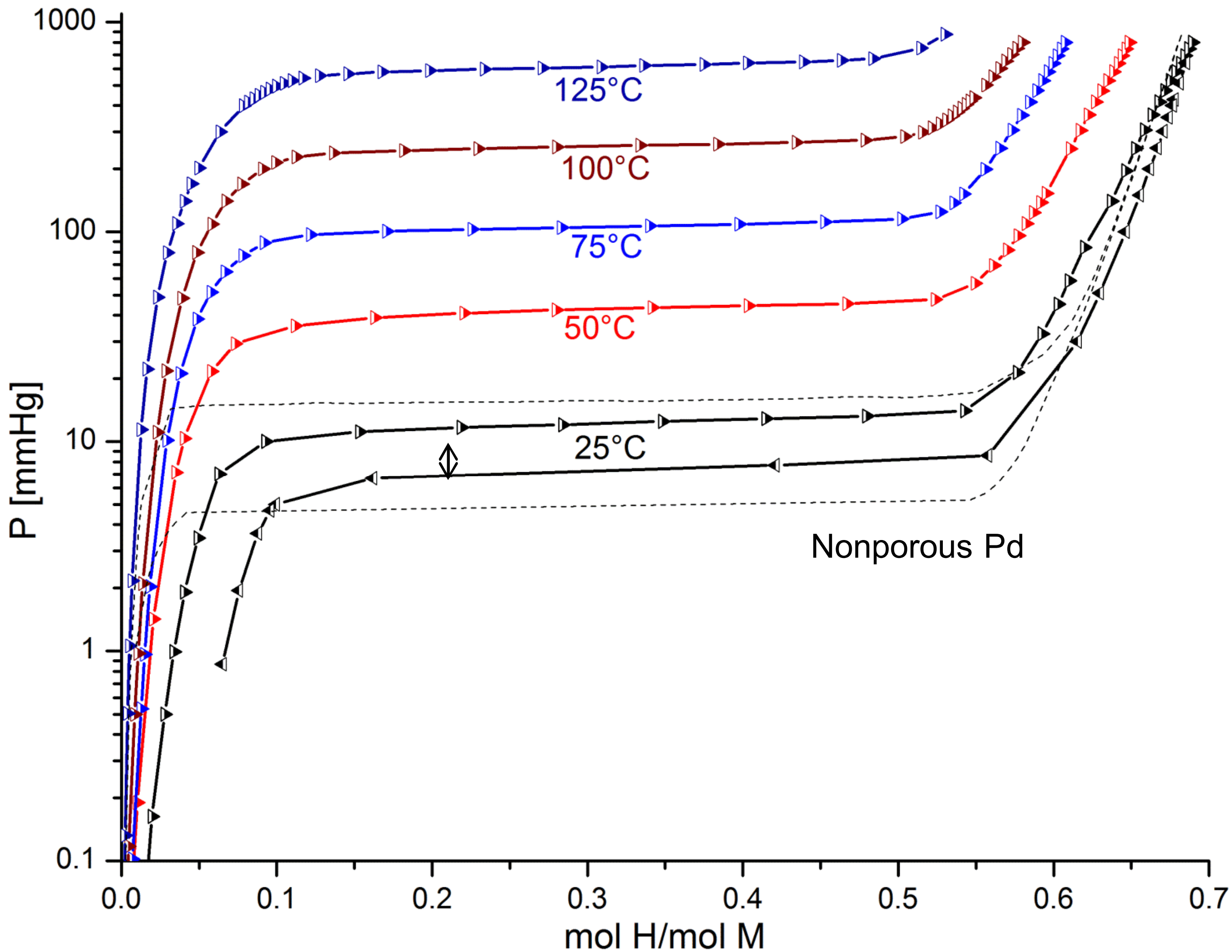
Nanoporosity improves properties

2) empty space in nanopores mitigates damage from cycling hydride

- Hysteresis (P_{abs} > P_{des}) in H_2 absorption/ desorption
- Nanopores reduce strain
- Deformation → dislocations, aging



Reduced Hysteresis in Nanoporous Pd



Synthesis of Nanoporous Pd

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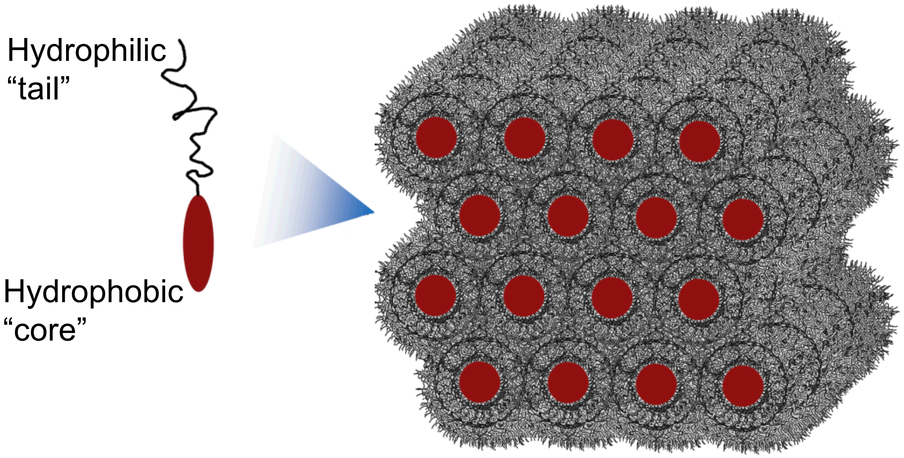
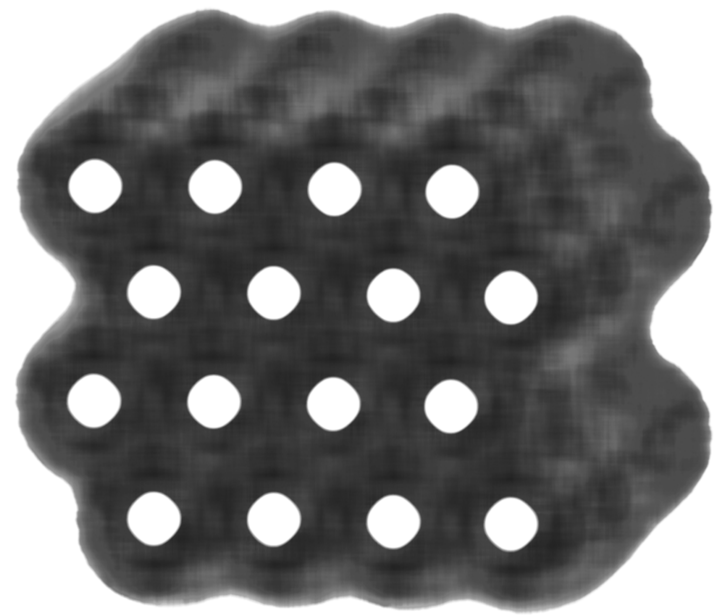


self-assembly into hexagonal array

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



yields nanoporous metal

- Adapted synthetic methods[1,2]:
  - Large quantities
  - Powders
  - *Control of pore size*
- Metal salts are reduced around hydrophobic cores
- Removal of template leaves nanoporous metal

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

Synthesis of Nanoporous Pd

bcp/Pd^{II} mixture

- $(NH_4)_2(PdCl_4)$ in H_2O
- (bcp-2.3,3.1k) in THF
- Solutions mixed, THF removed by evaporation (THF = tetrahyrofuran)

reduced paste

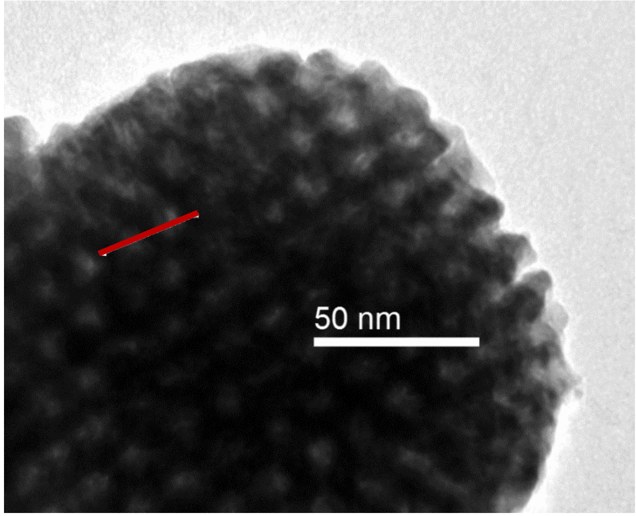
- Resulting paste reduced over 48 hours in humidified 1% H_2 in N_2

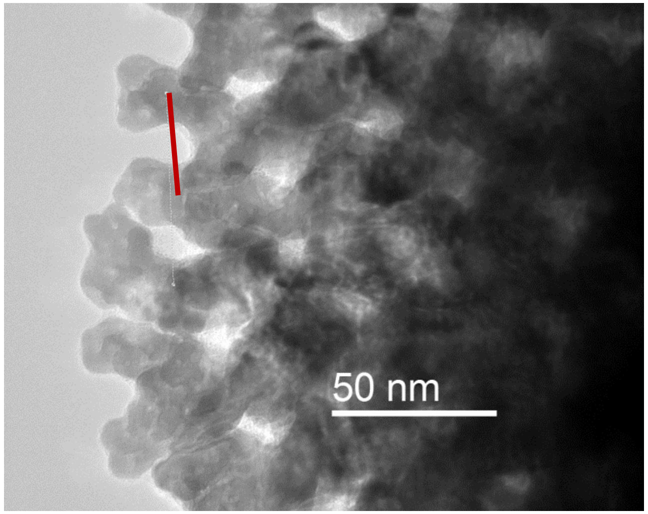
bcp-Pd

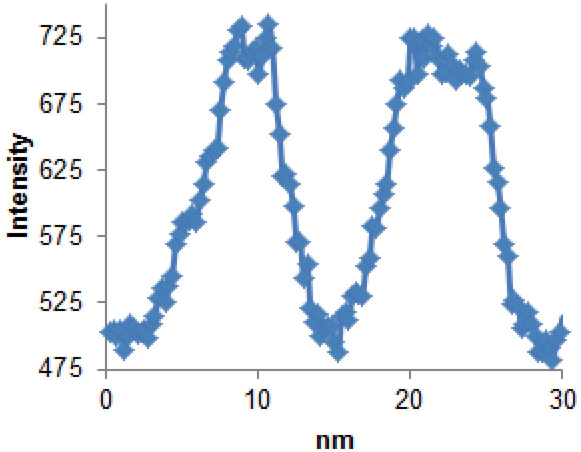
- Reduced paste dissolved in THF/H_2O
- Free-flowing powder after removal of bcp-2.3,3.1k with solvent wash

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

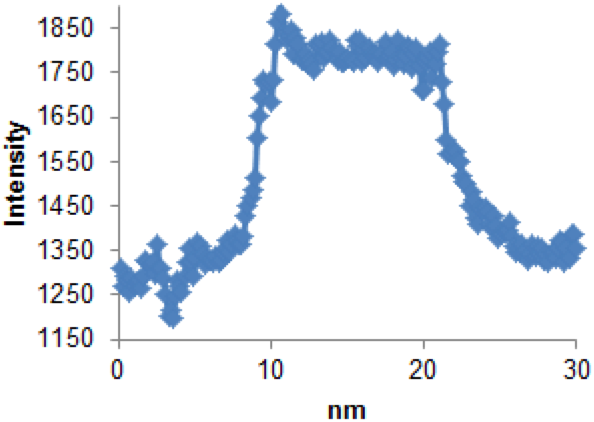
Tunable pore size







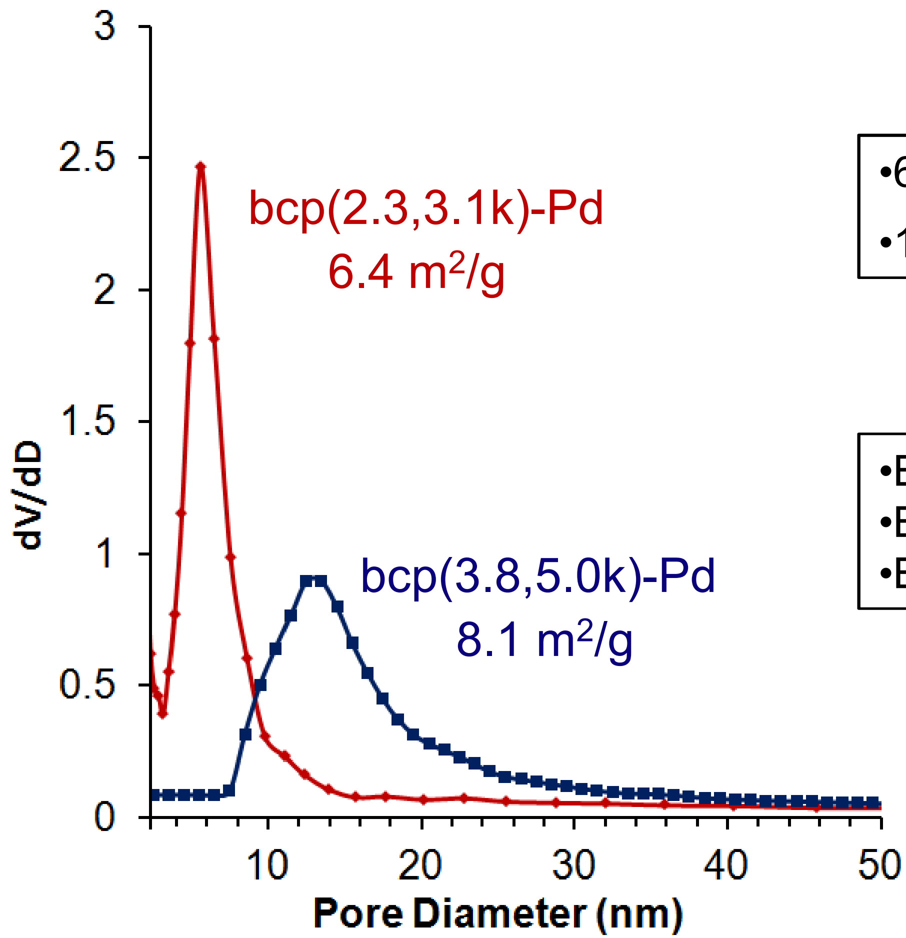
bcp(2.3,3.1k)-Pd
15 nm pitch
7 nm pore



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

Tunable pore size

Bulk-scale measurements corroborate TEM measurements

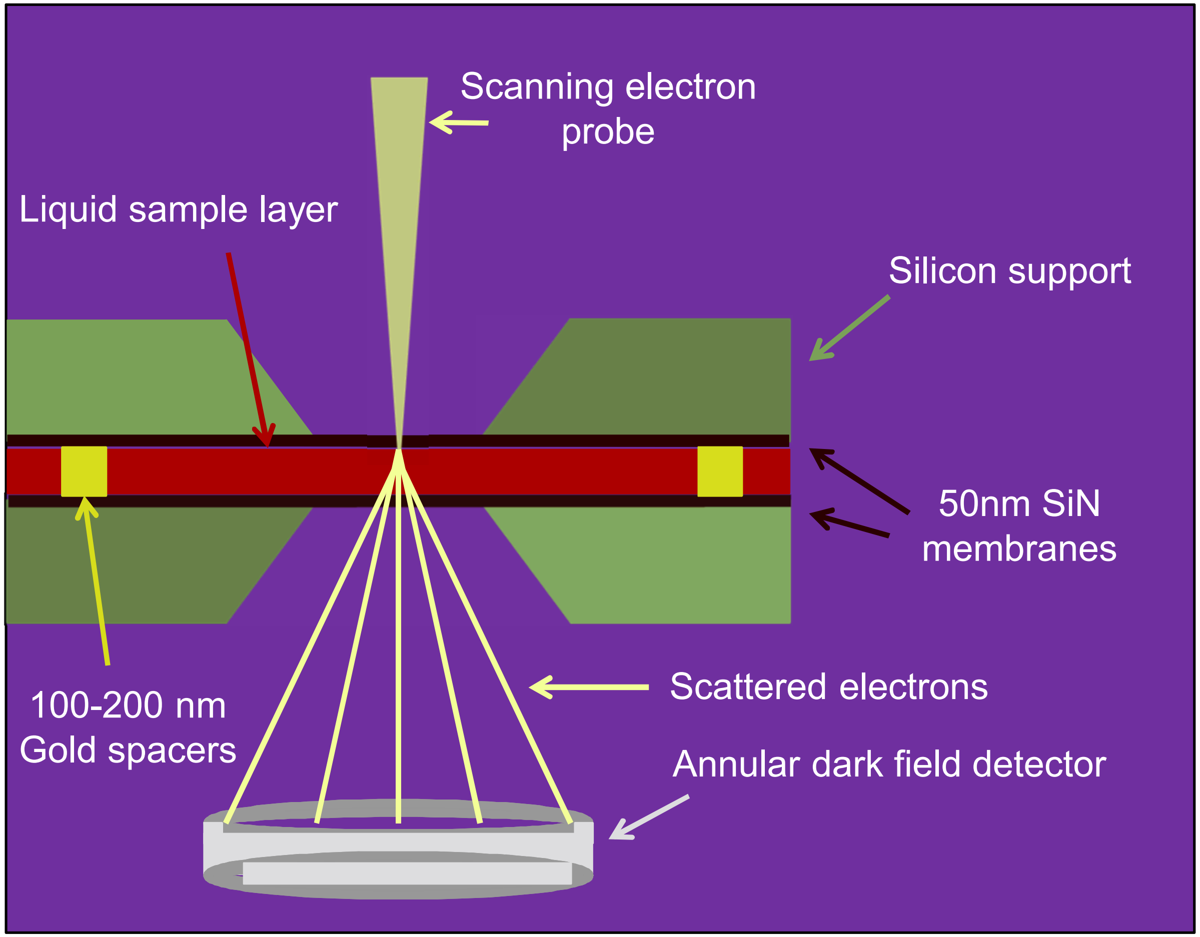


- 6-8 nm maximum for small pore
- 12-14 nm for large pore

- Based on N_2 isotherms at 77K
- BET Surface Area
- BJH Pore Size Distribution

Synthesis in TEM liquid stage

Pd salt, block copolymer, water; e-beam is reducing agent



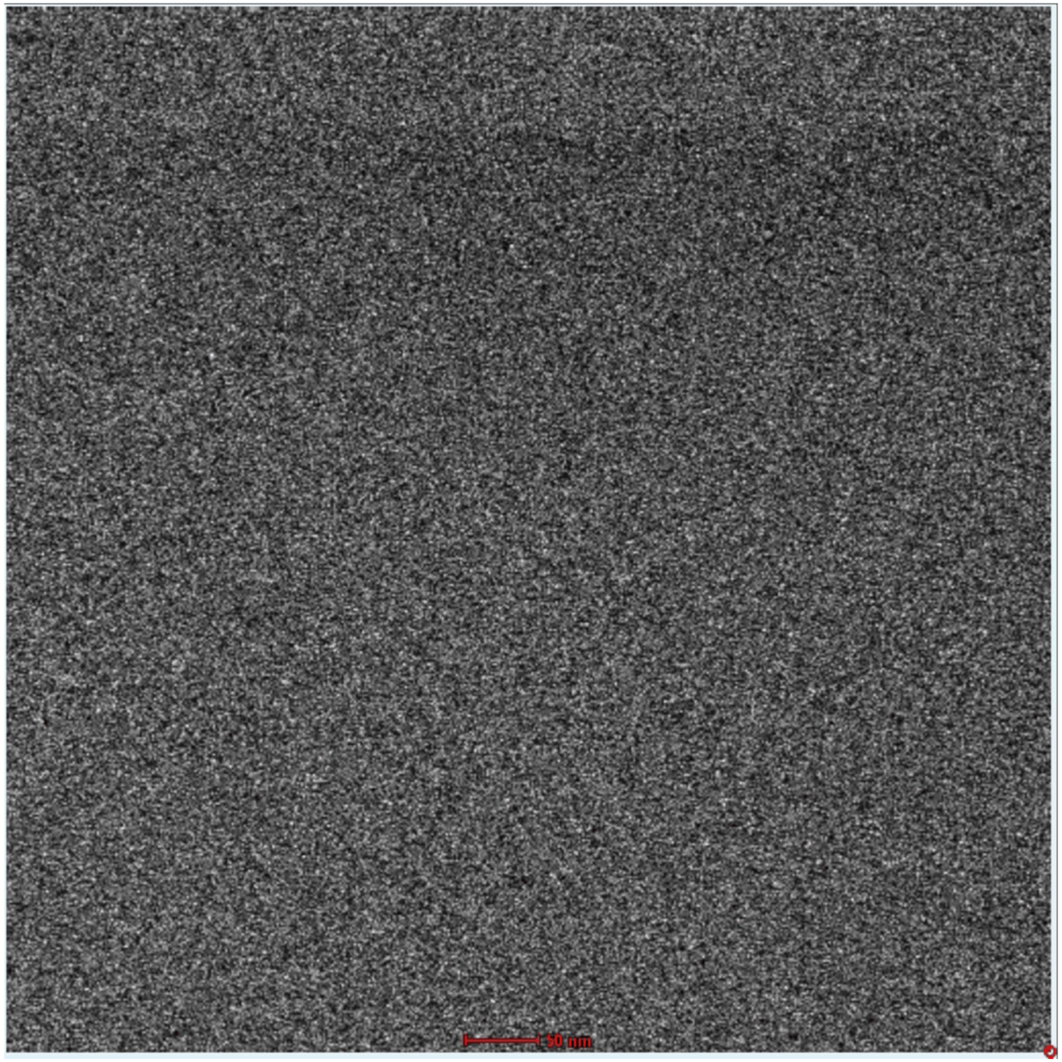
Parent *et al*., ACS Nano, 2012, 6, 3589
Parent *et al*., Chem. Mater. 2014, 26, 1426

Synthesis in TEM liquid stage

Nanoparticles nucleate, grow, and fuse to form porous structure

Too much solvent leads to pore disorder

Parent *et al.*, Chem. Mater. 2014, 26, 1426

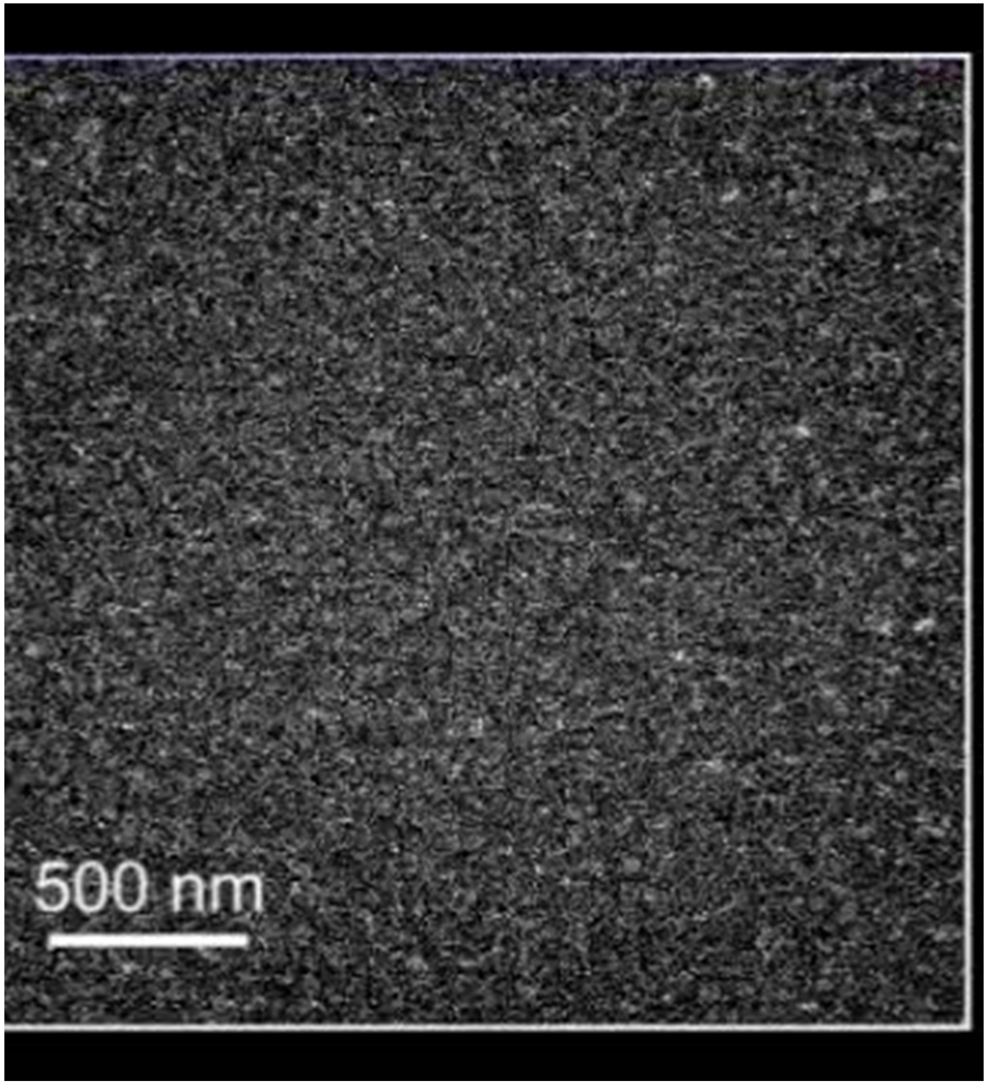


Synthesis in TEM liquid stage

Nanoparticles nucleate, grow, and fuse to form porous structure

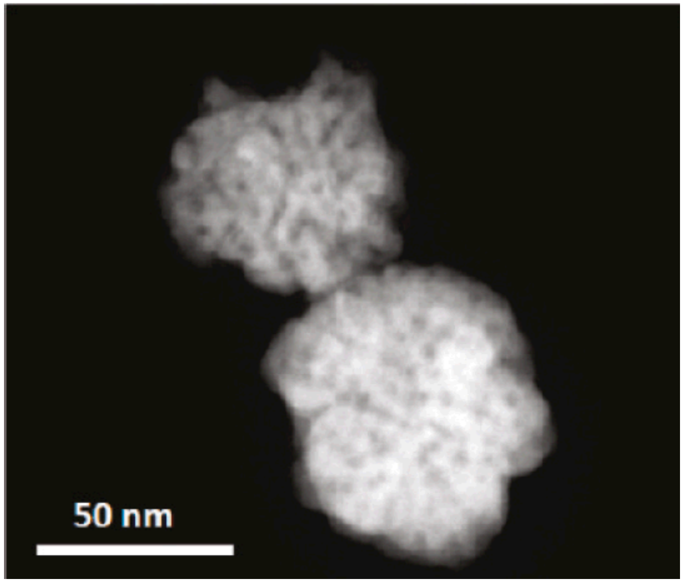
Solvent vapor anneal improves ordering

Parent *et al*., Chem. Mater. 2014, 26, 1426

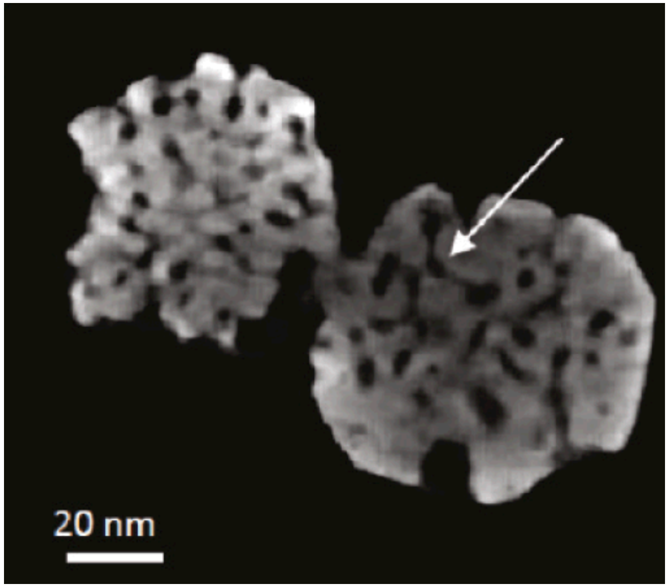


Small pores coarsen upon heating

3 nm pores



Room Temperature



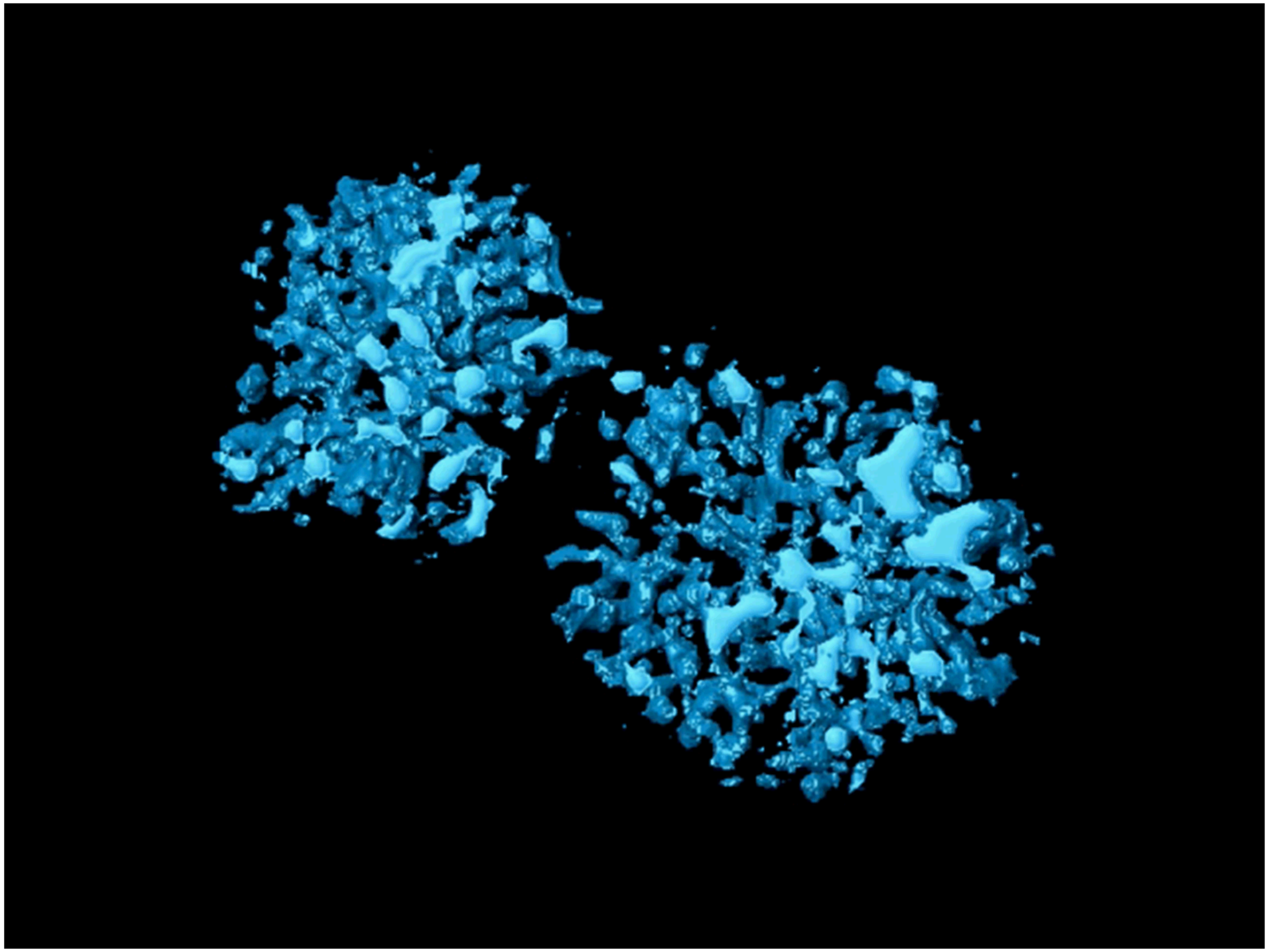
600°C

- 3 nm pores obtained with small-molecule surfactant, PEG_{10} hexadecyl ether
- STEM and STEM-tomography show that pores begin to collapse at 200°C.
- By 600°C, pores have coalesced into large voids.
- Larger pores should be more stable.

Robinson *et al*., Int. J. Hydrogen Energy 2009, 34, 5585-5591
Klein, *et al*., J. Am. Chem. Soc. 2011, 133, 9144–9147

3D pore structure

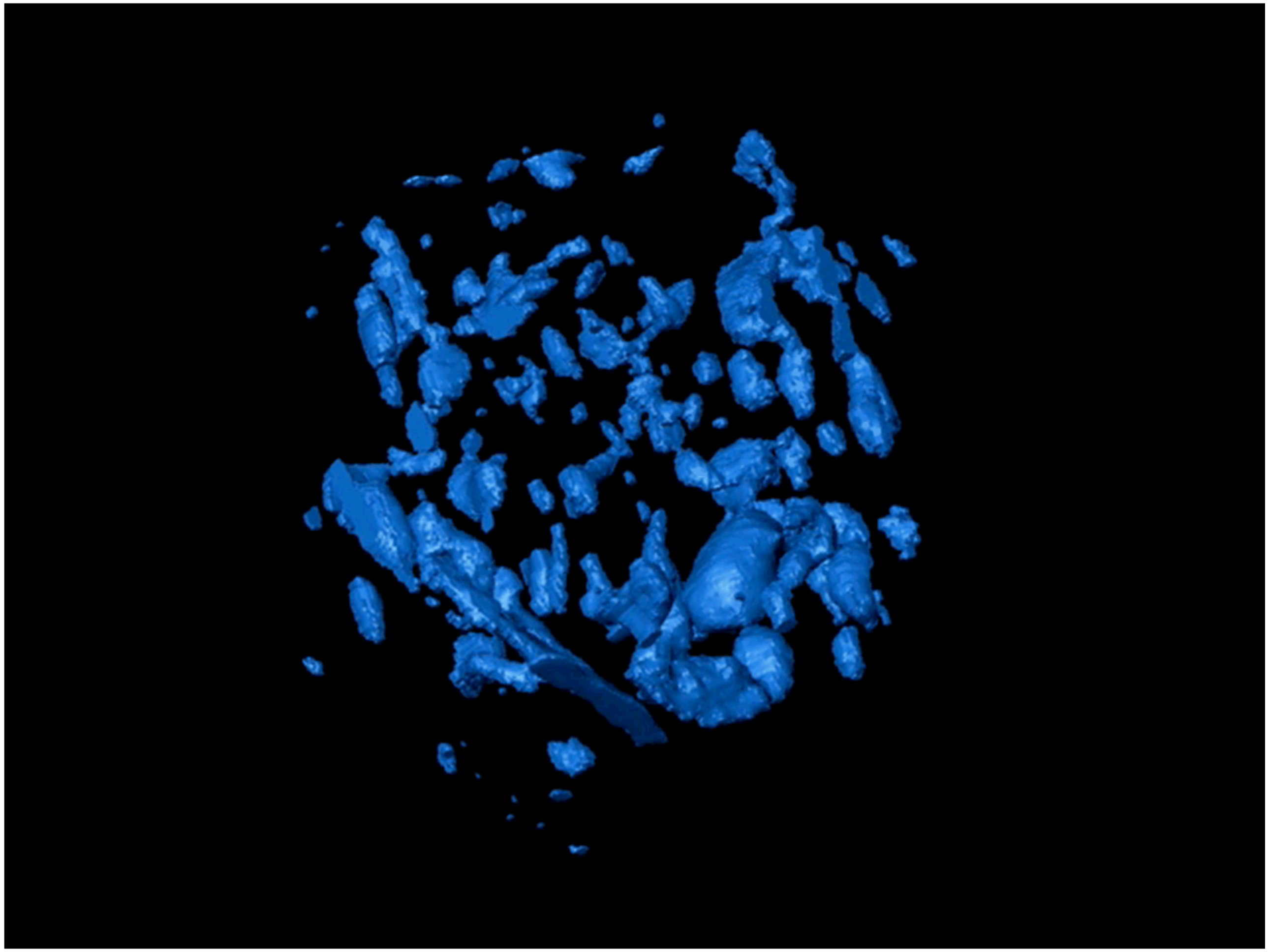
Pore junctions
coarsen at
200 C



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

3D pore structure

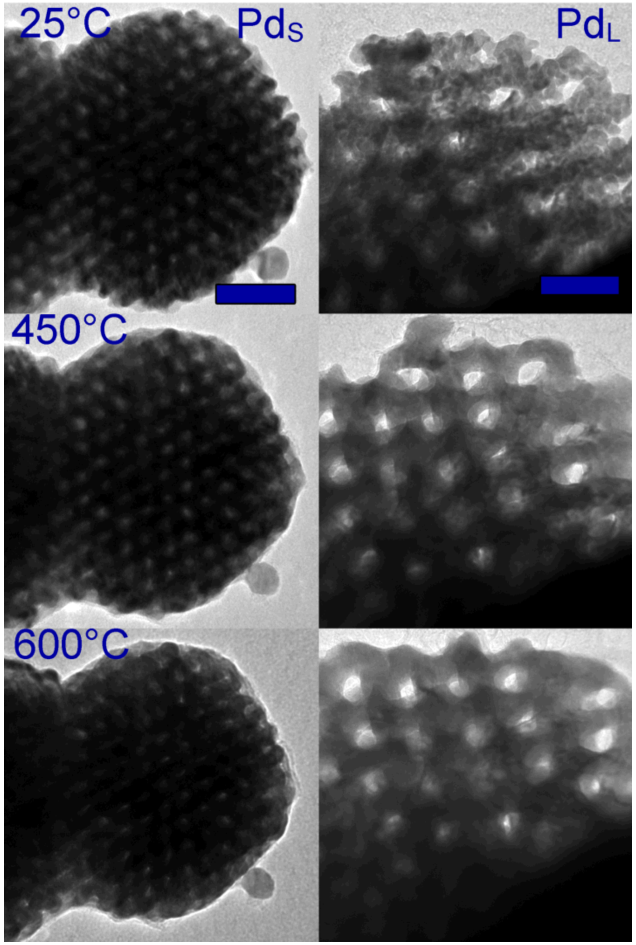
Pores collapse to bubbles at 600 C

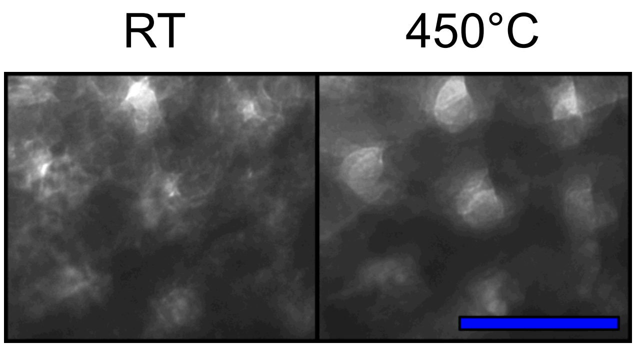


Klein, *et al.*, J. Am. Chem. Soc. 2011, 133, 9144–9147

Larger pores are more stable

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 intact

50 nm scalebars

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

H_2 environment decreases stability

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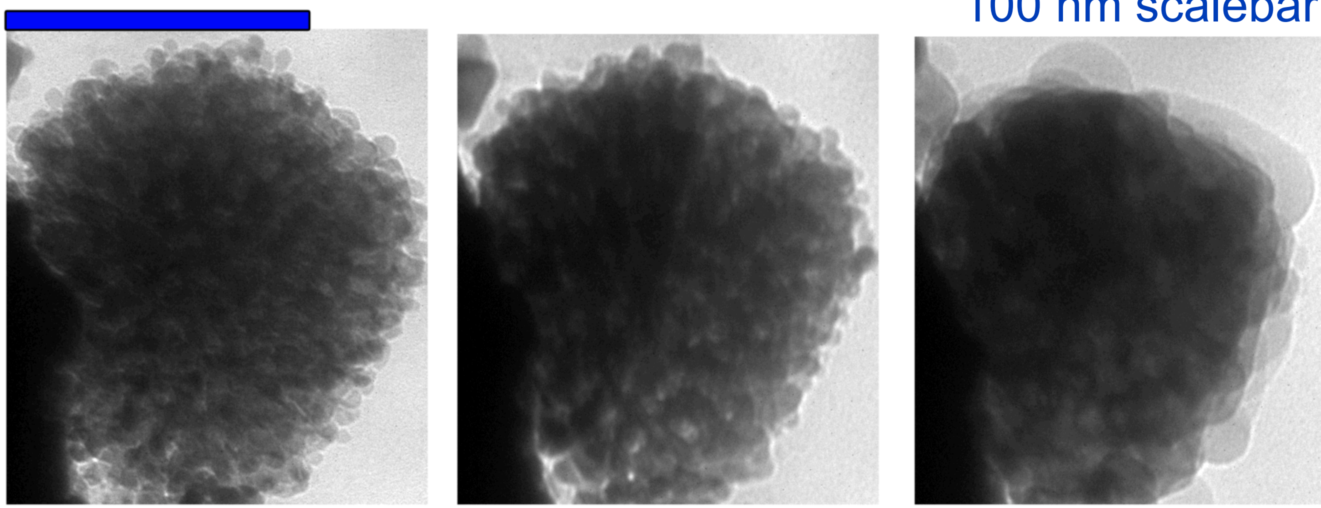
TEM images at 125°, under 1 atm H_2 after several pulses to specified temperature

100 nm scalebar



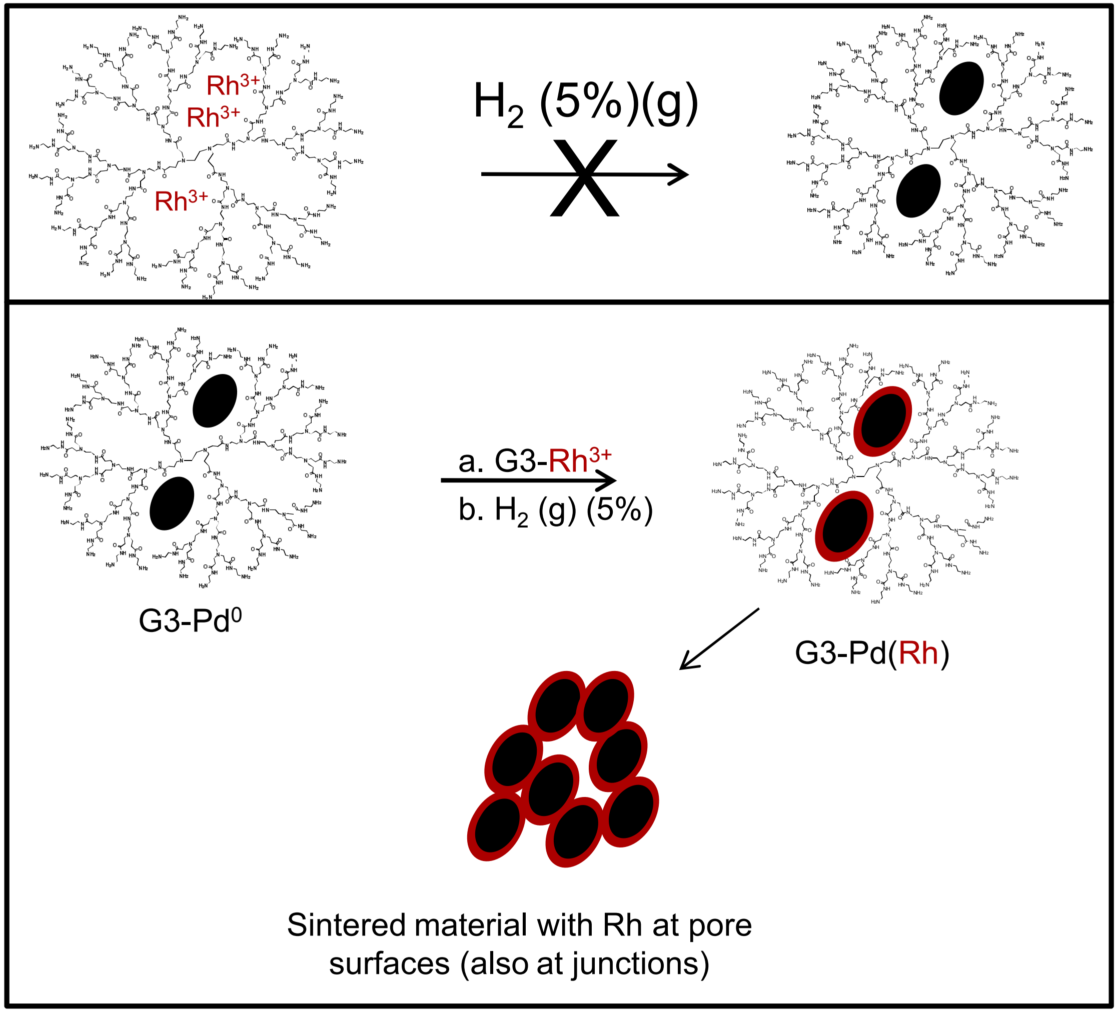
125°C 200°C 300°C

Possible factors contributing to decreased stability:

- Contraction from dehydriding
- Surface state

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

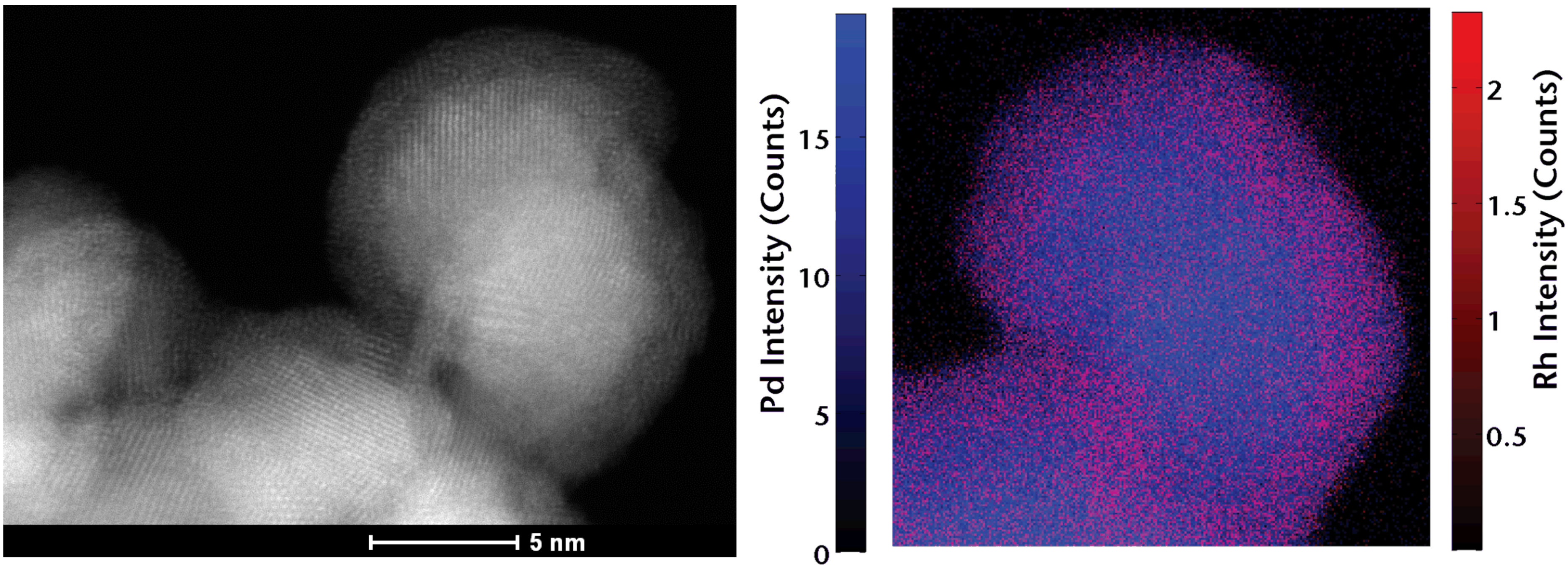
Surface coatings for thermal stability



Cappillino *et al*. J Mater. Chem. 2012, 22, 14013-14022

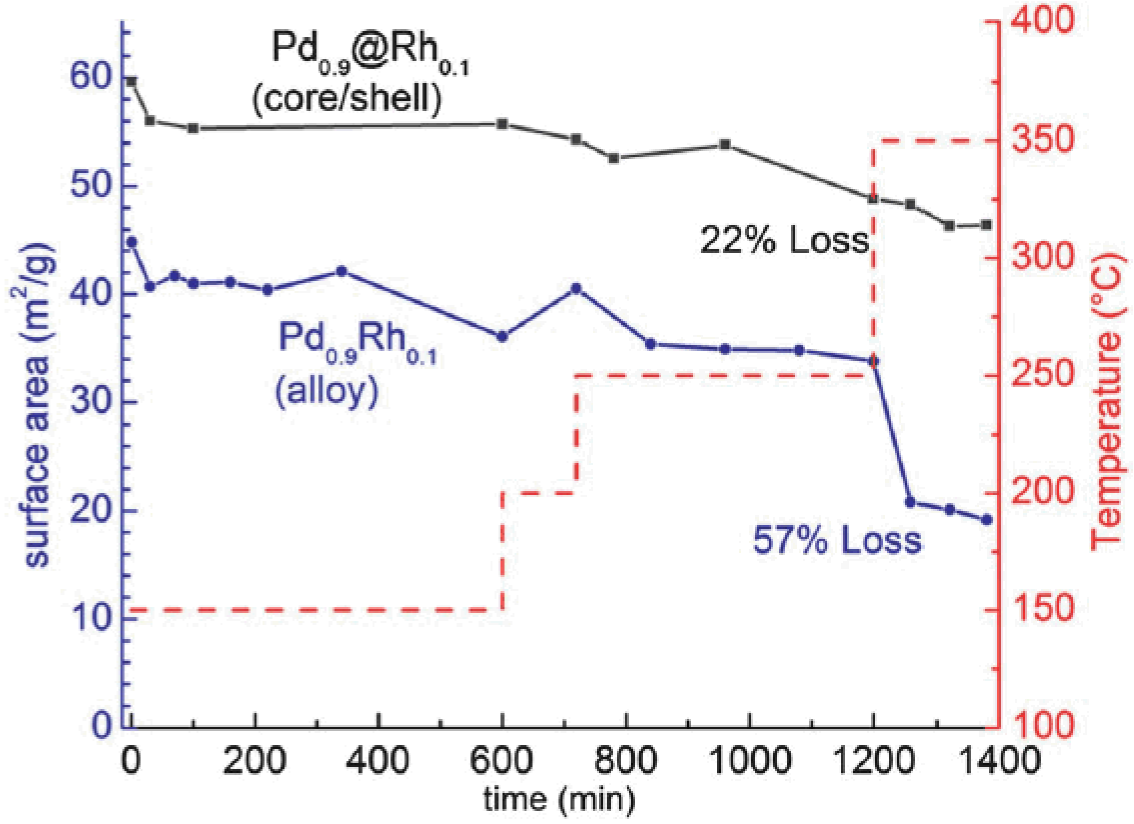
Crooks, Richard M., *et al.* J. Am. Chem. Soc. 2004, 126, 15583-15591

Uniform Rh coating



Cappillino *et al*. J Mater. Chem. 2012, 22, 14013-14022

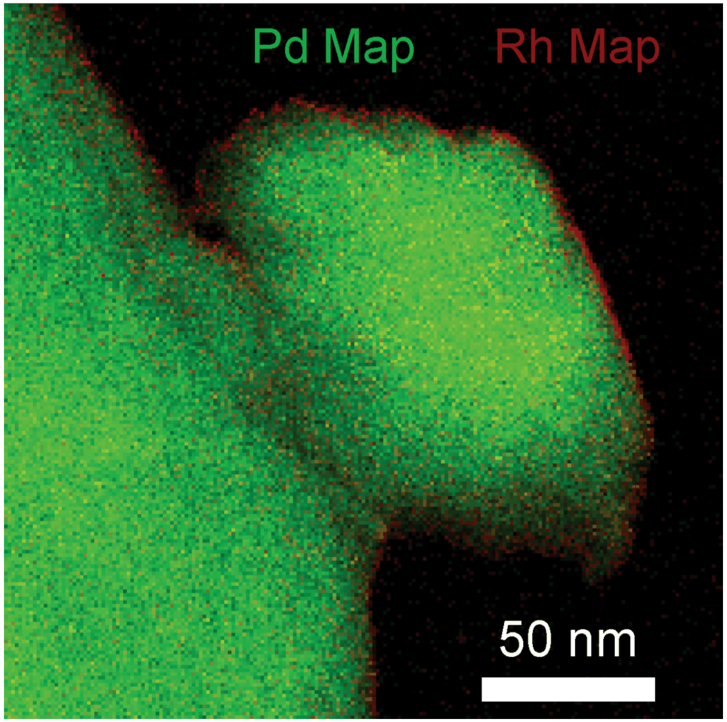
Core-shell is more stable than alloy



Cappillino *et al*. J Mater. Chem. 2012, 22, 14013-14022

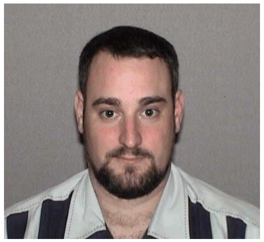
Atomic-layer electroless deposition

- We have recently developed a method to deposit monolayers of metal onto arbitrarily shaped noble metal substrates.
- New path to thermal stability
- Pt too

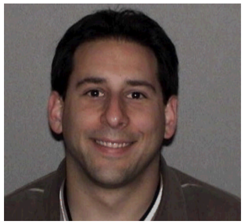


Cappillino *et al*. Langmuir 2014, 30, 4820-4829

Contributors



Pat Cappillino
Block copolymers



Josh Sugar
EDS imaging

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Protochips, Inc.
In situ TEM (heated)

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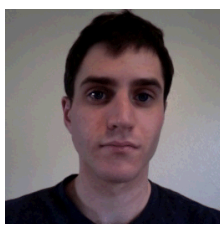
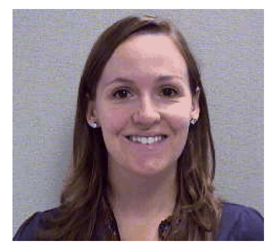
Ilke Arslan
Pacific Northwest National Lab
Liquid cell TEM

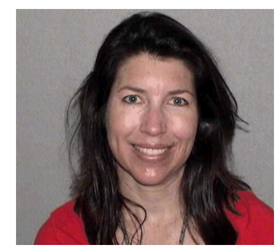


Lucas Parent
UC Davis
Liquid cell TEM

Khalid Hattar
In situ TEM (H_2)



Blythe Clark
In situ TEM (H_2)



Michelle Hekmaty
TEM/EDS

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Bonus slides

Particle size control

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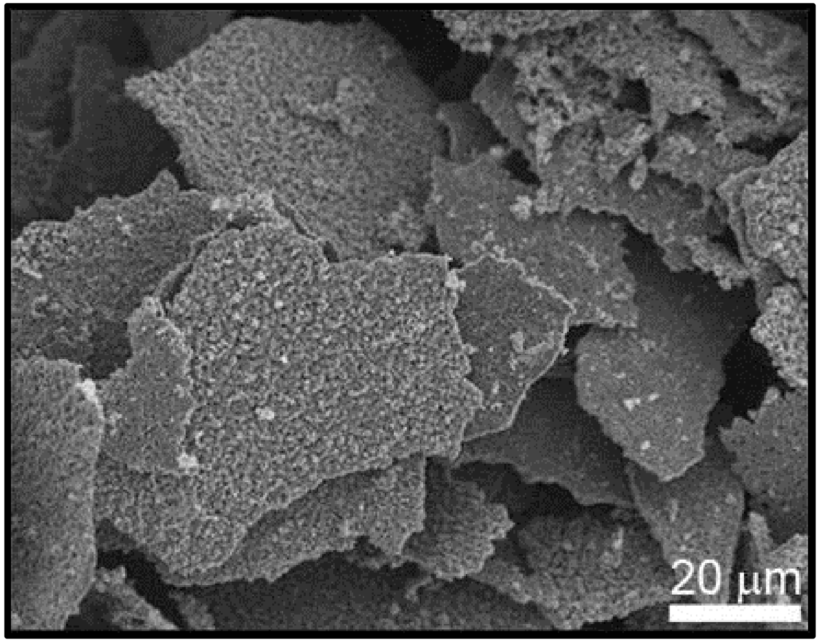
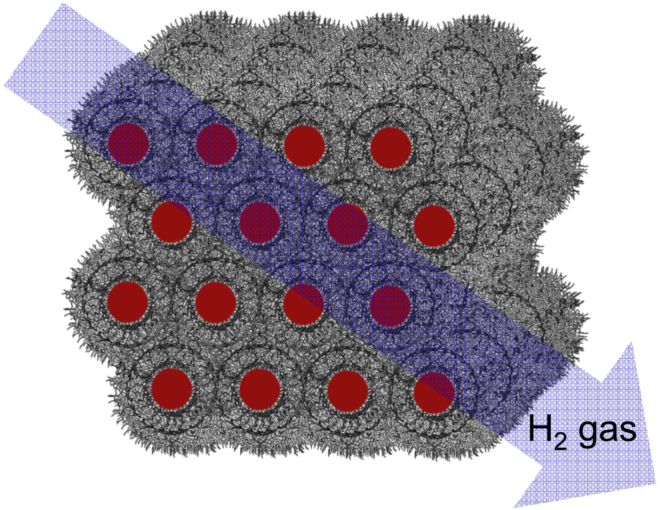
Must Control ***Particle*** Size as well as pore size



Irregular particle shapes
and sizes affect gas flow

H_2 gas as reductant

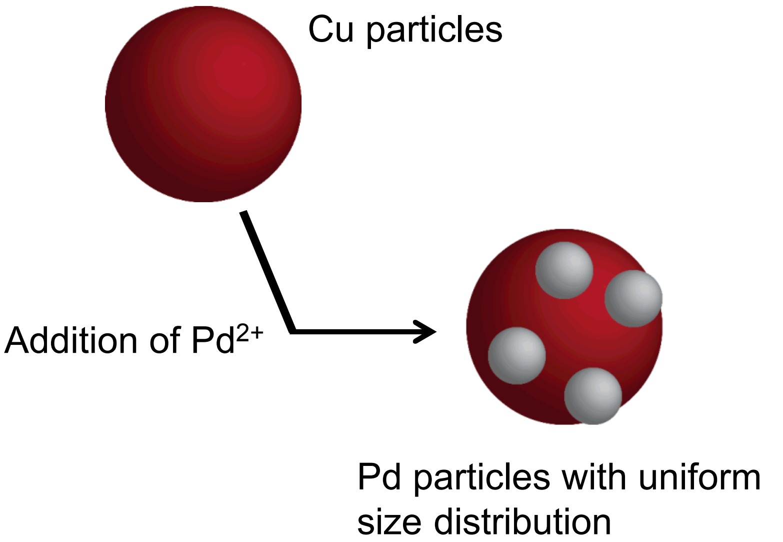


- Homogenous reduction reaction occurs
- No mechanism for control of growth at particle scale

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

Locally constrained reductant dose

Galvanic displacement of Cu^0 by Pd^{2+}



X.F. Lu et al., Sci. Adv. Mater. 2010, 2, 413-320

Pd particles replicate Cu particles

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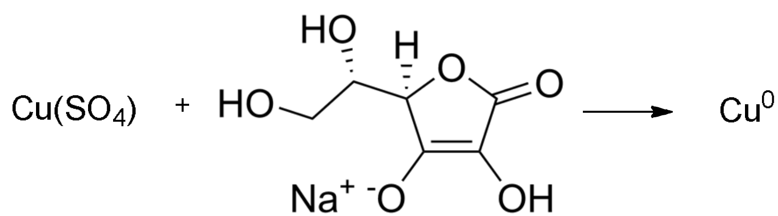
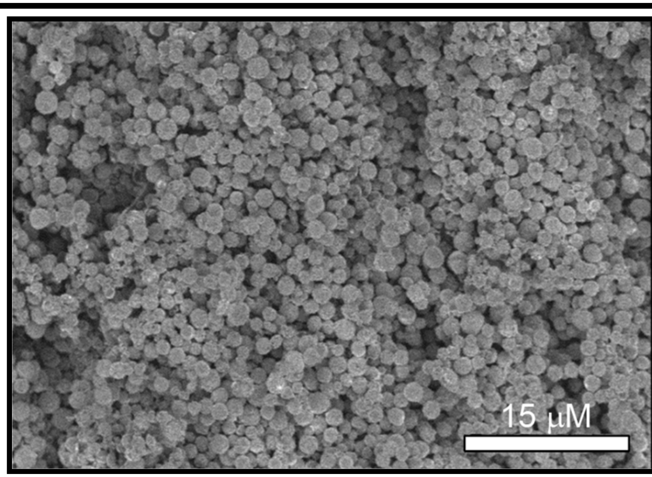
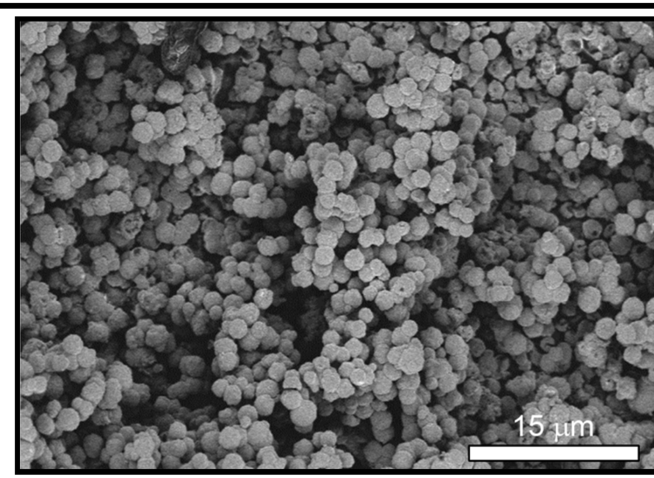
- Nonporous Cu particles made by reduction of $Cu(SO_4)$ with sodium ascorbate
  - Suspension added to $(NH_4)_2PdCl_4$ in dilute block copolymer solution



$$Cu^0 + Pd^{2+} \longrightarrow Pd^0$$

Cu particles

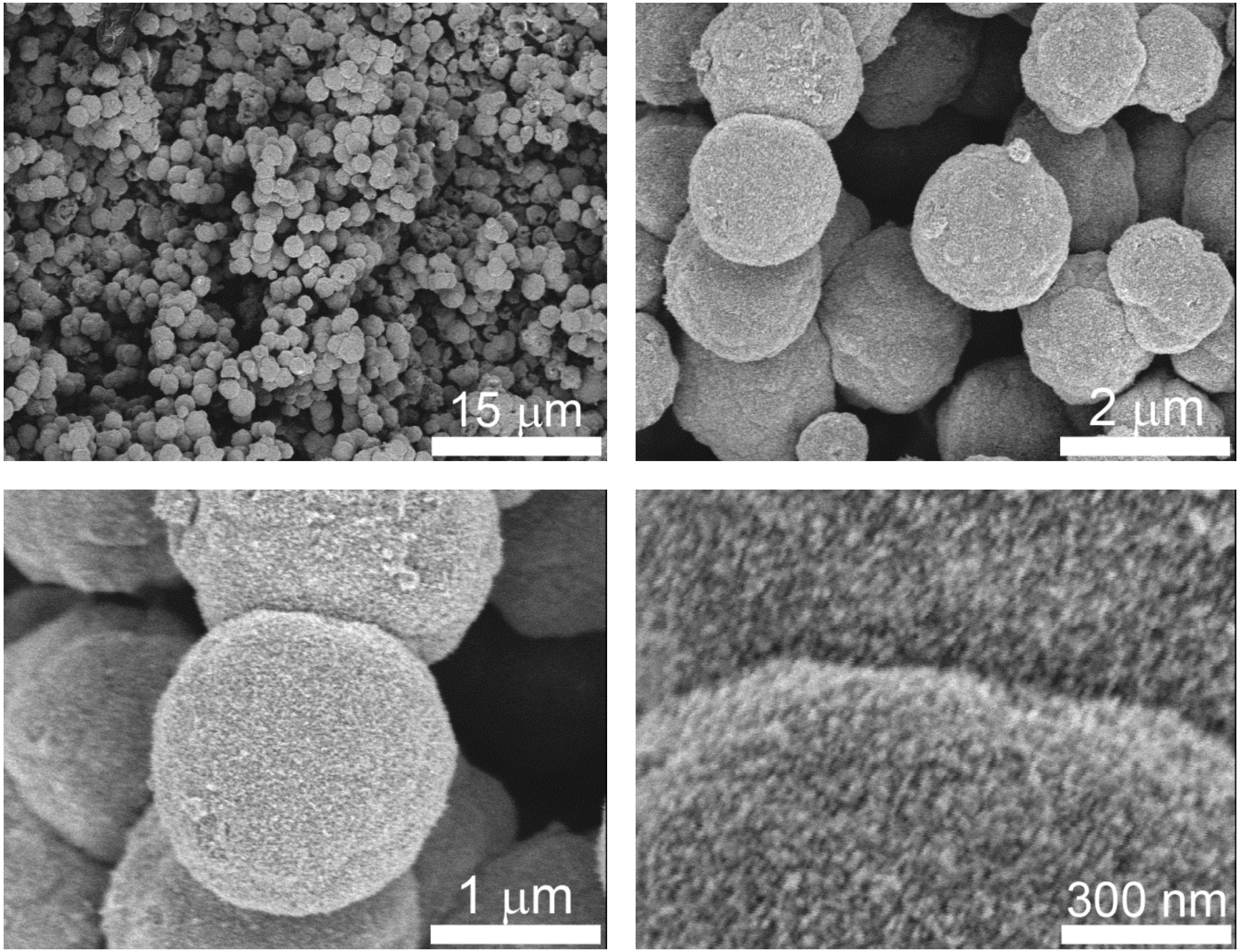




Pd particles

Jones et al., Powder Tech. 2014, 267, 95-102.

Defined pore, particle size



Jones et al., Powder Tech. 2014, 267, 95-102.