

Exceptional service in the national interest



Surfactant-Templated Nanoporous Metal Films and Powders

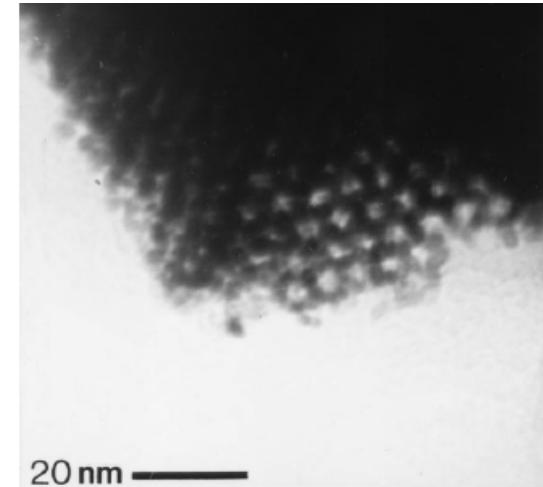
Presented by David B. Robinson
Electrochemical Society Meeting
May 2015



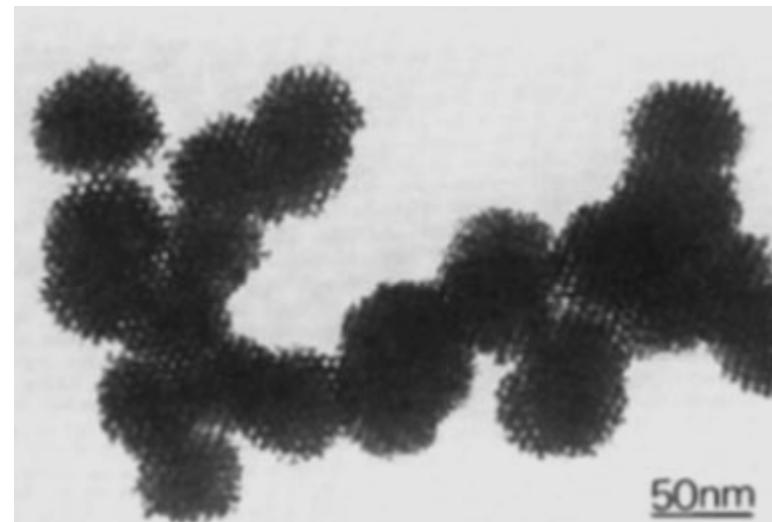
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND NO. 2011-XXXXP

Early templated porous metals

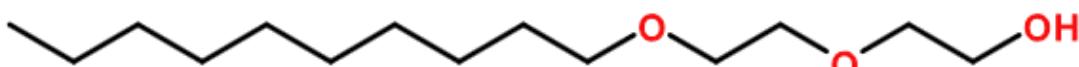
- Attard et al., Science 278 838 (1997)
- Extended work on porous silica
- Aqueous H_2PtCl_6 plated in 42% C_{16}EO_8 →
- $20 \text{ m}^2/\text{g}$
- Applications: supercapacitors, catalysts



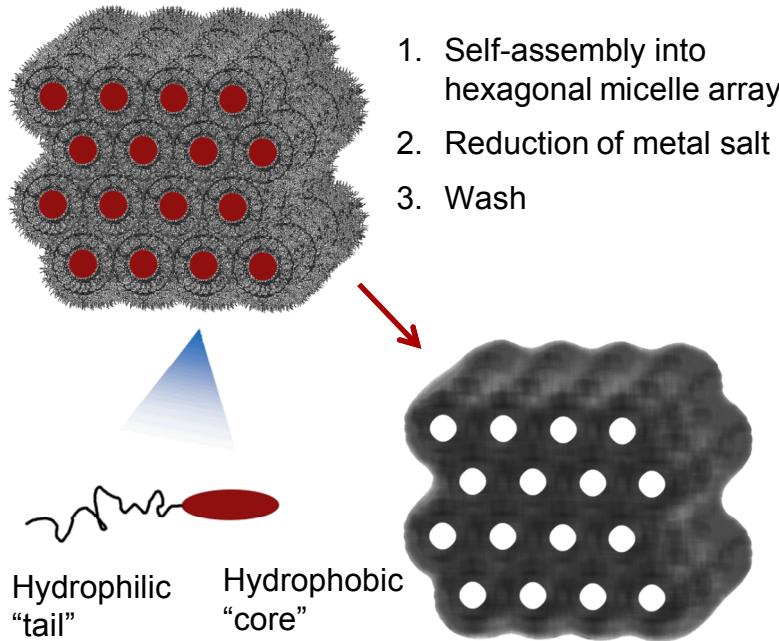
- Attard et al.,
Angew. Chem. 36 1315 (1997)
- N_2H_4 -reduced Pt particles →



C_{10}EO_2 surfactant:



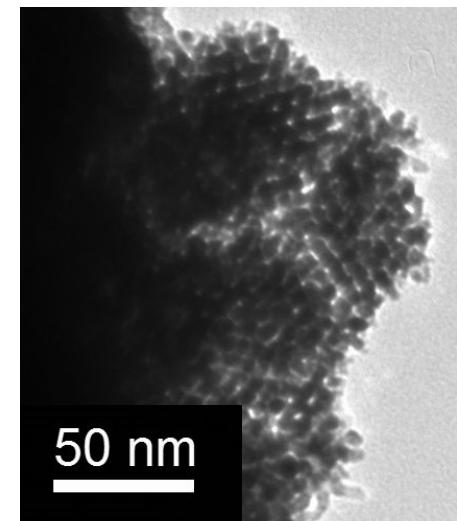
Reduction in lyotropic liquid crystals



1. Self-assembly into hexagonal micelle array
2. Reduction of metal salt
3. Wash

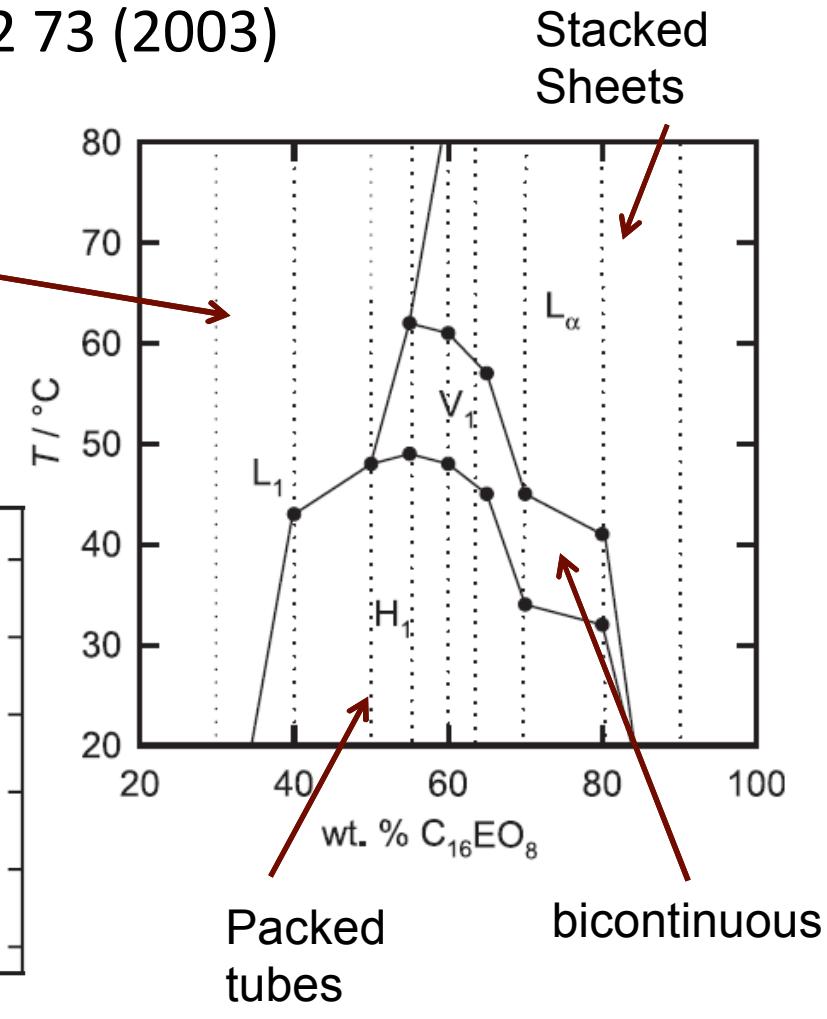
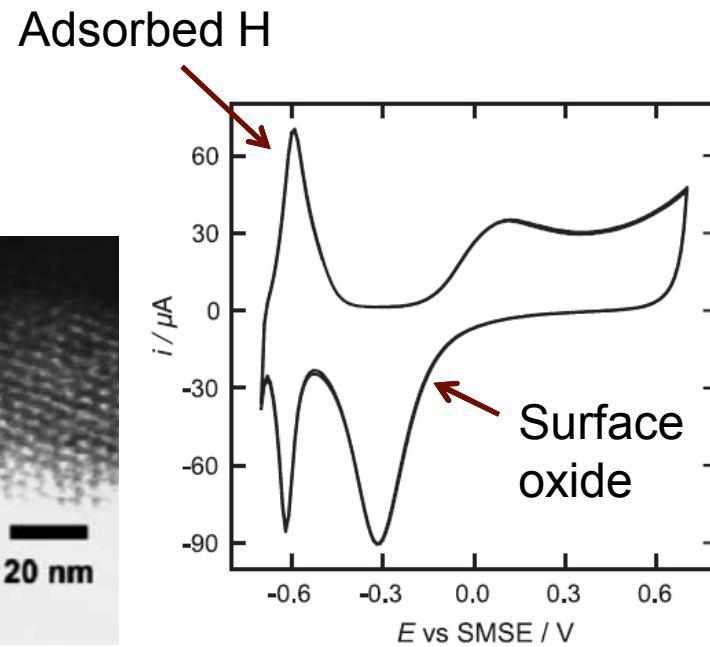
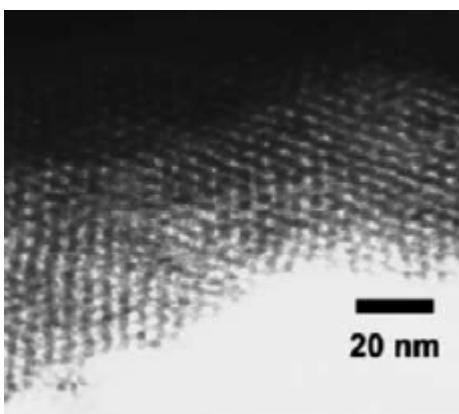


- Robinson et al.,
Int. J. Hydrogen Energy 35 5423 (2010)
- Particles grow around surfactant phase
- Pd and PdRh alloys



Plating in lyotropic liquid crystals

- Bartlett and Marwan,
Microporous Mesoporous Mater 62 73 (2003)
- Heptane swelling agent
- Electroplated Rh
- $30 \text{ m}^2/\text{g}$



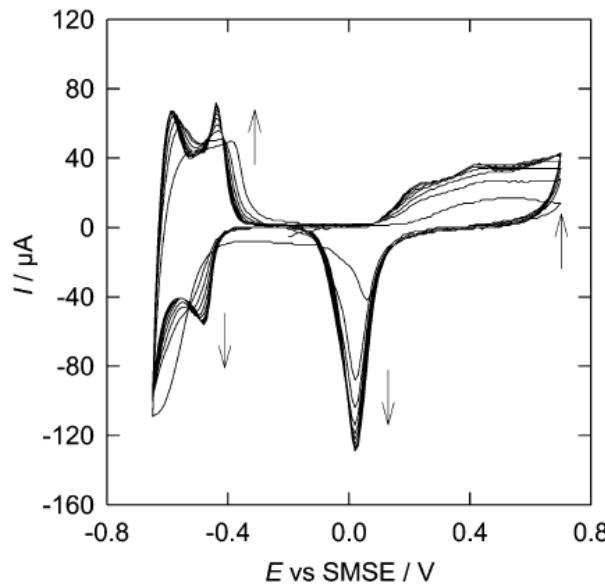
Surfactant removal

- Can require long soaks

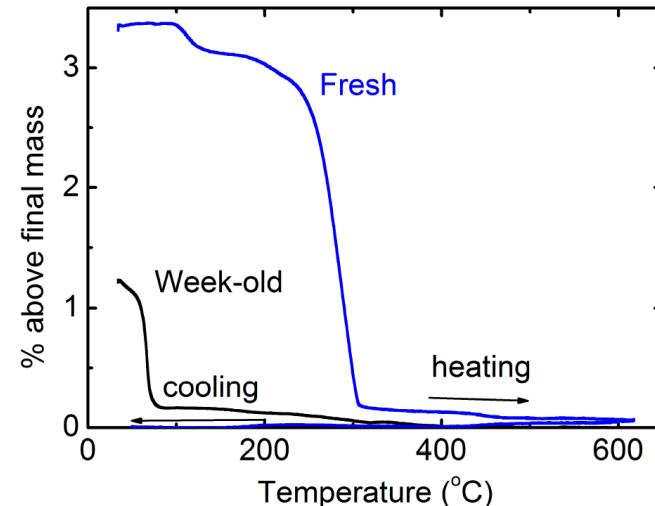
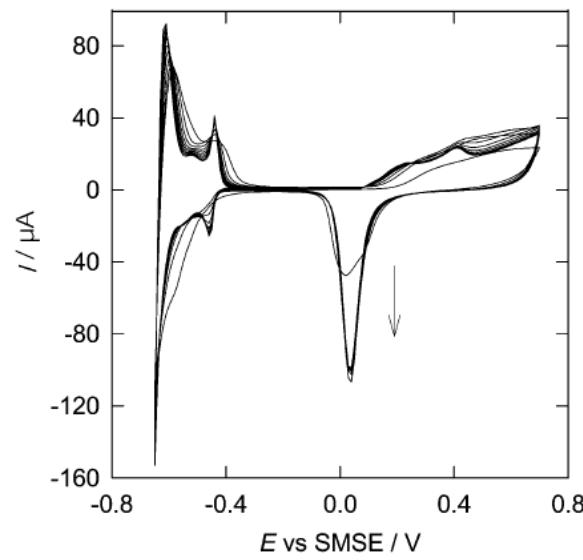
Bartlett et al.,
Phys. Chem. Chem. Phys. 4 3835 (2002)

200 nm Pd film from Brij 56 (impure $C_{16}EO_8$)
- Surfactant residue impacts electrochemical kinetics

10 min water soak



60 min water soak



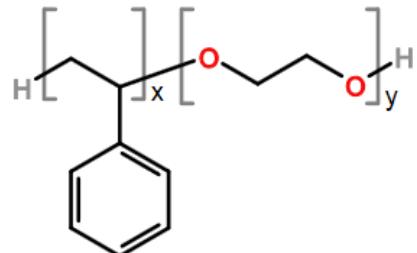
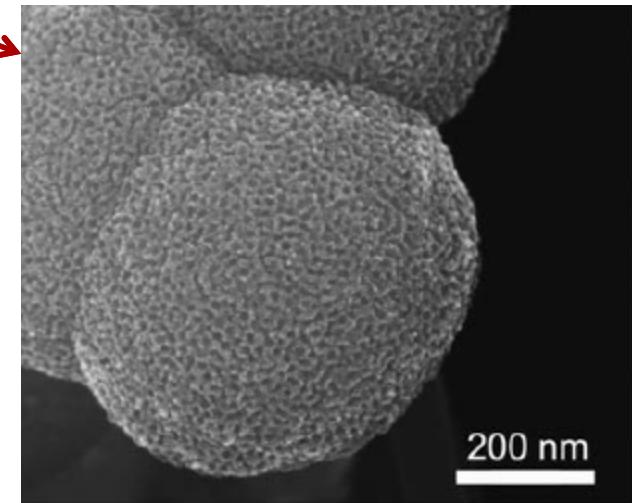
- Easier with oxidized surfaces

Ong et al.
Chem Mater. 24 996 (2012)

Pd:Rh 9:1
4h ethanol-water soak

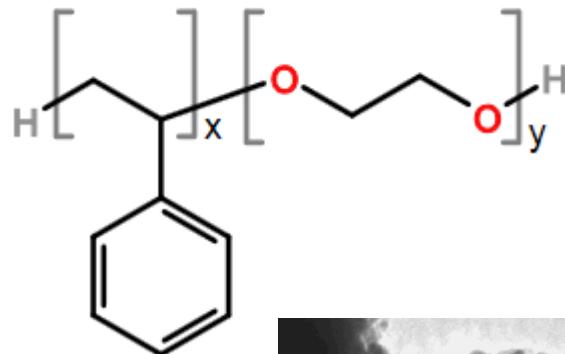
Block copolymer gels

- Pt films from Block copolymer gels
Yamauchi et al., Angew. Chem. 47 5371 (2008)
Takai et al., JACS 132 209 (2010)
- Pore size in SEM range
- Gram scale, H_2 -reduced Pd
Cappillino et al.
J. Mater. Chem. A 1 602 (2013)

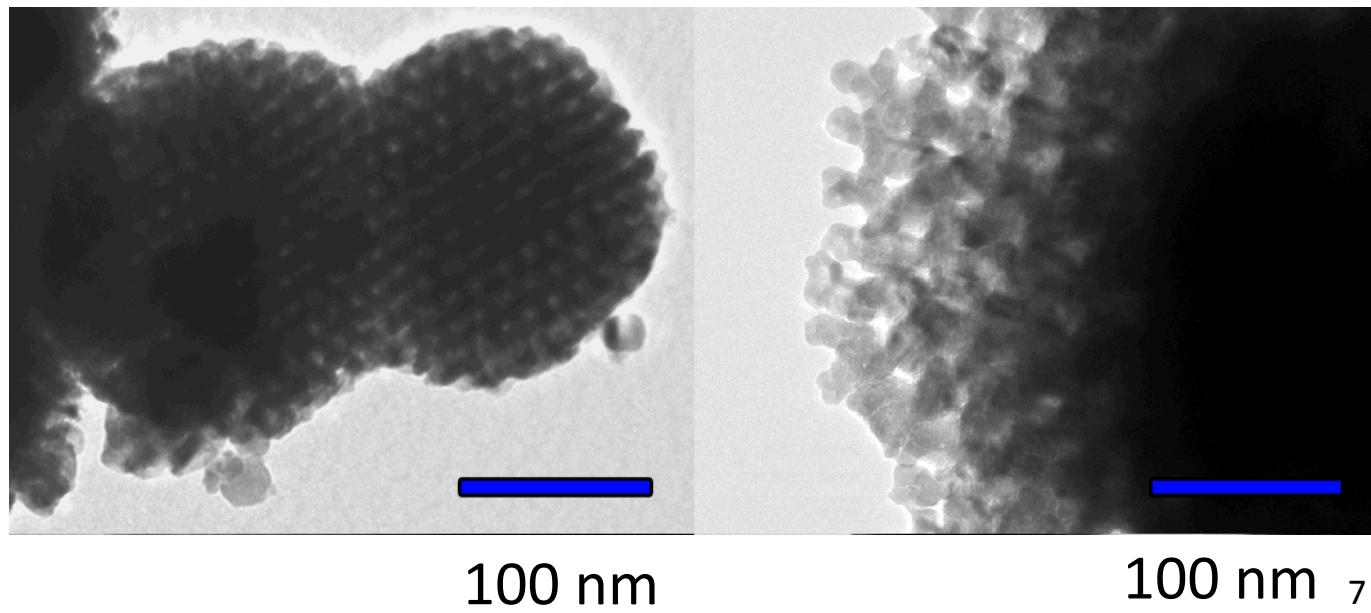


Size tuning with block copolymers

- Cappillino et al. J. Mater. Chem. A 1 602 (2013)
- Poly (styrene-block-ethylene oxide)

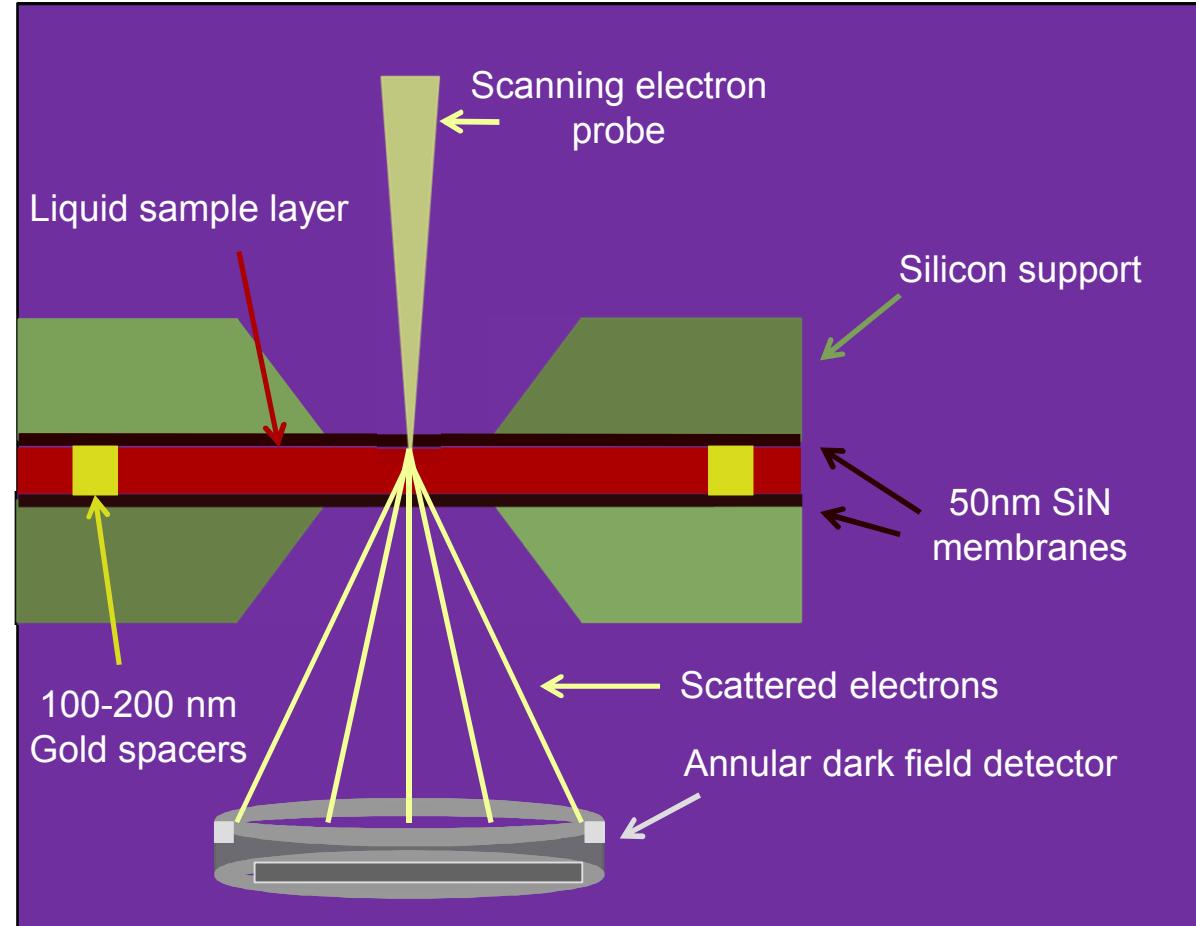


Name	x	y	Pore, nm	Pitch, nm
Pd _S	22	70	7	15
Pd _L	36	113	12	30



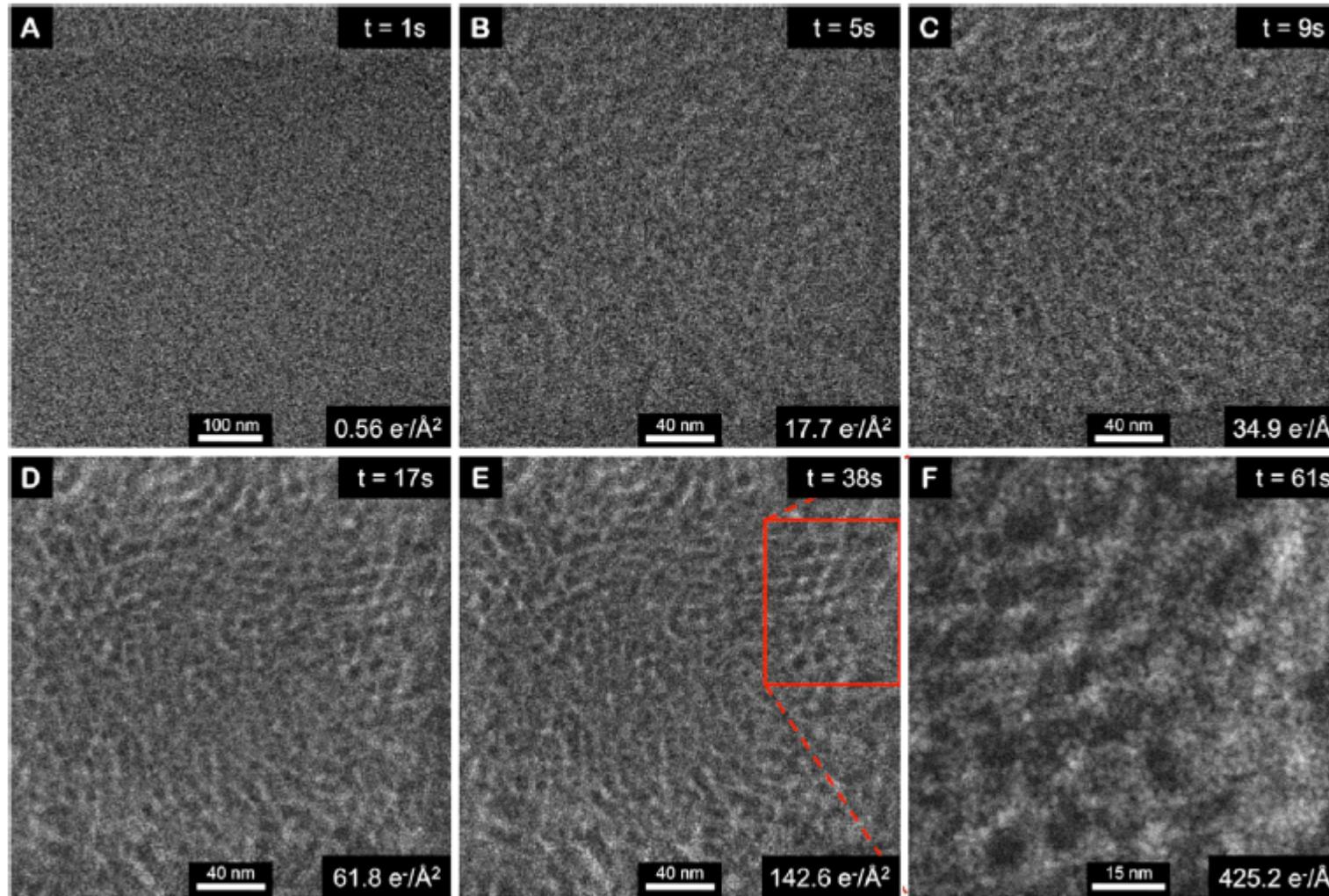
Liquid cell electron microscopy

- Electron beam reduced Pd
- Gel dropcast into cell
- Parent et al.,
Chem. Mater.
26 1426 (2014)



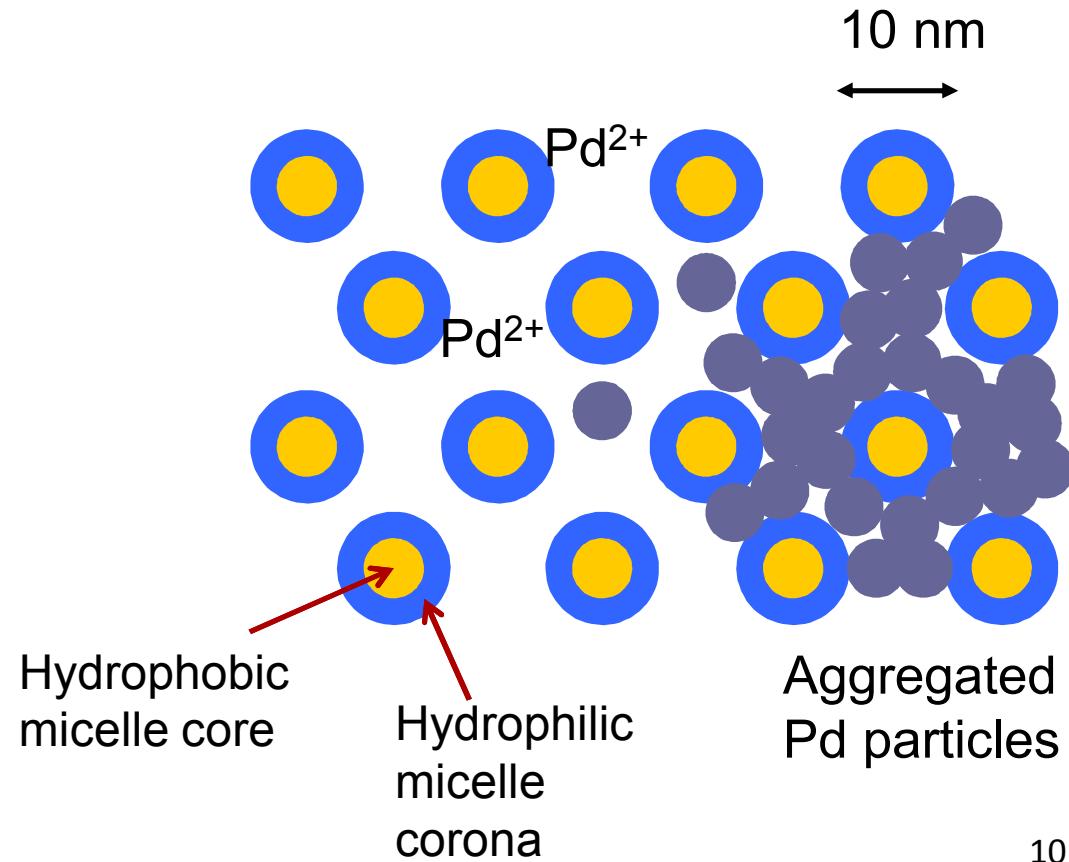
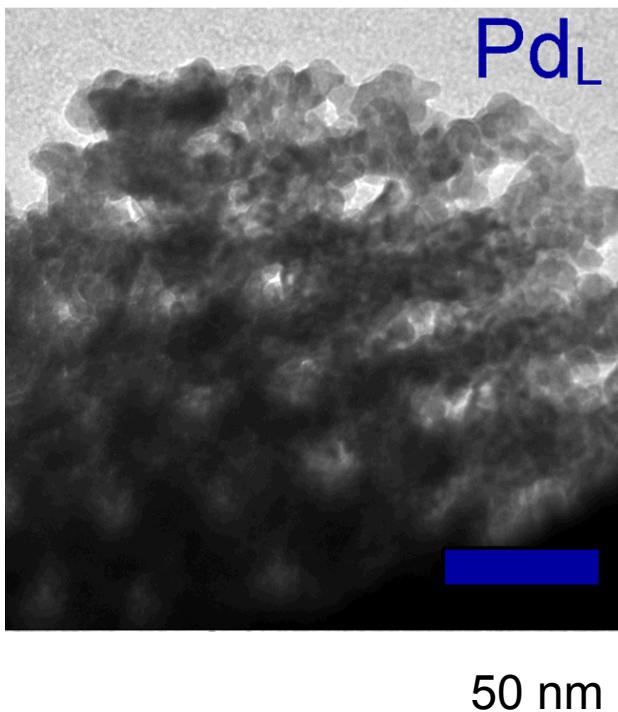
Liquid cell electron microscopy

- Bulk reduction: nucleation, aggregation, sintering

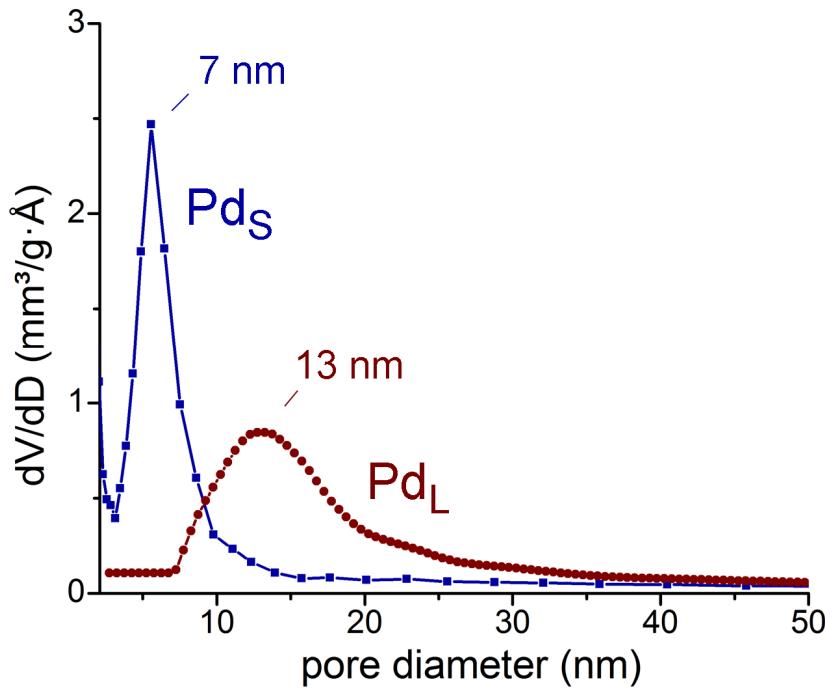


Chemical reduction: mechanism

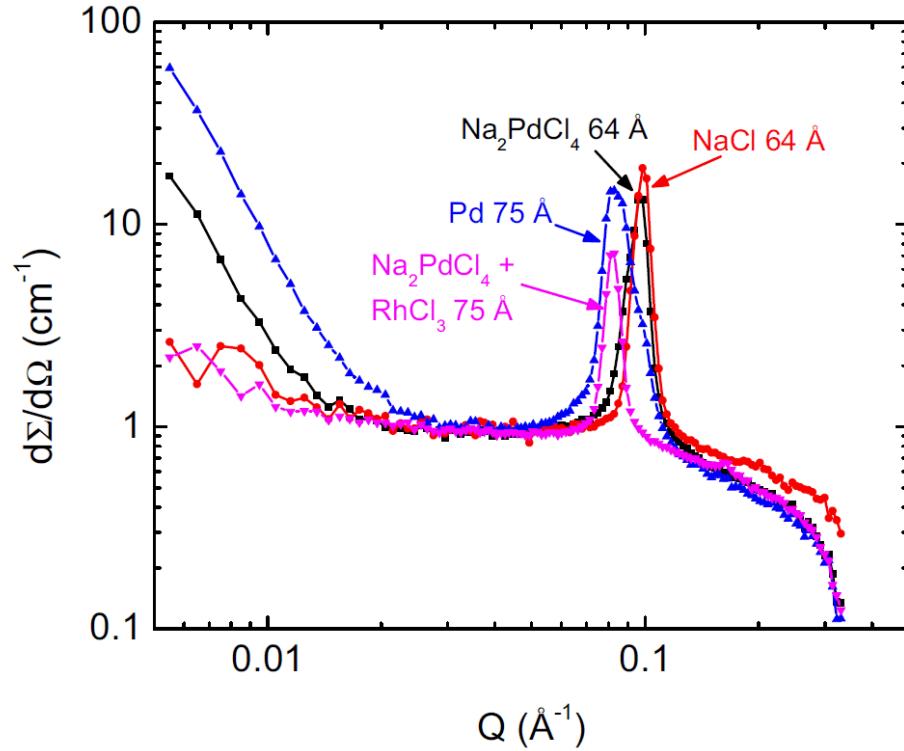
- Particles nucleate, then aggregate around micelles
- Overgrowth results in loss of porosity



Bulk measurements corroborate EM



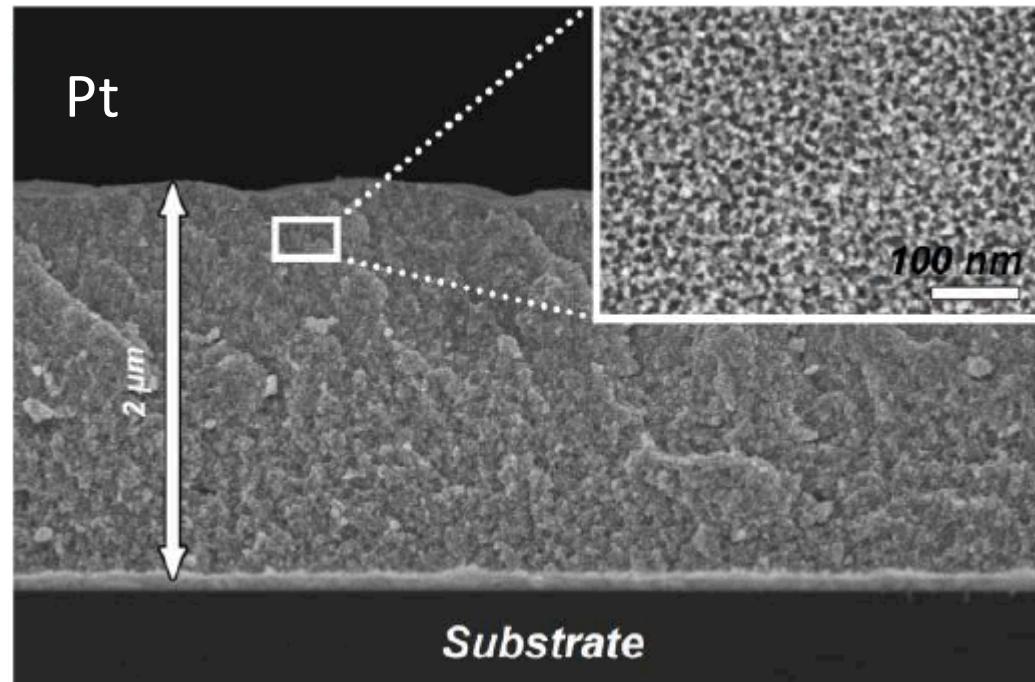
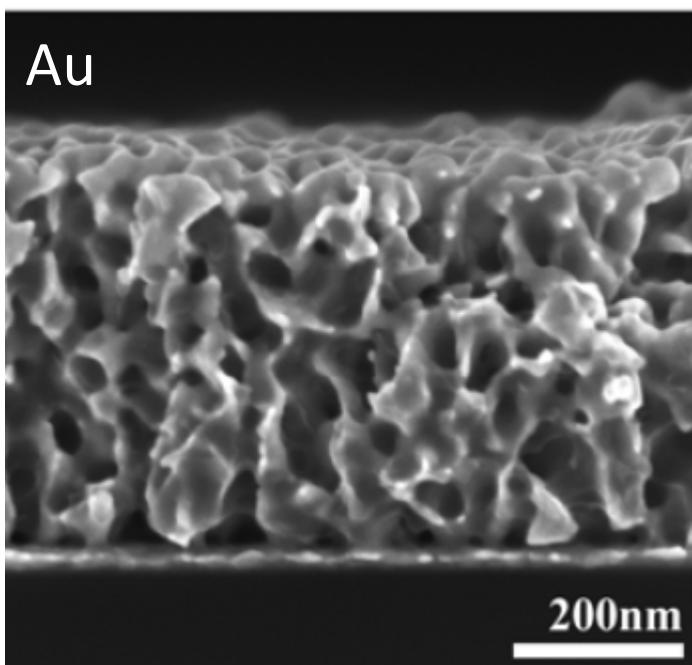
N_2 porosimetry shows pore size
PS-PEO block copolymer
J. Mater. Chem. A 1 603



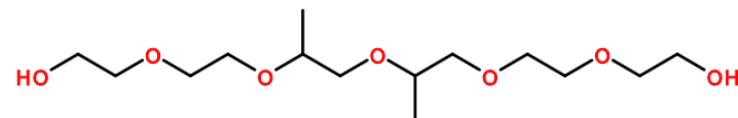
Neutron scattering shows
micelle spacing at various
stages of reaction
 $C_{16}EO_8$ (Brij 56)
I. J. Hydrogen Energy 35 5423

Plating from dilute micellar phase

- Eliminates slow, messy pastes, gels; pores less ordered
- Pt + F127: Wang et al., Chem. Mater. 24 1591 (2012)
- Au + PS-PEO: Li et al., Nature Comm. 6 6608 (2015)
 - Uses mixed solvent

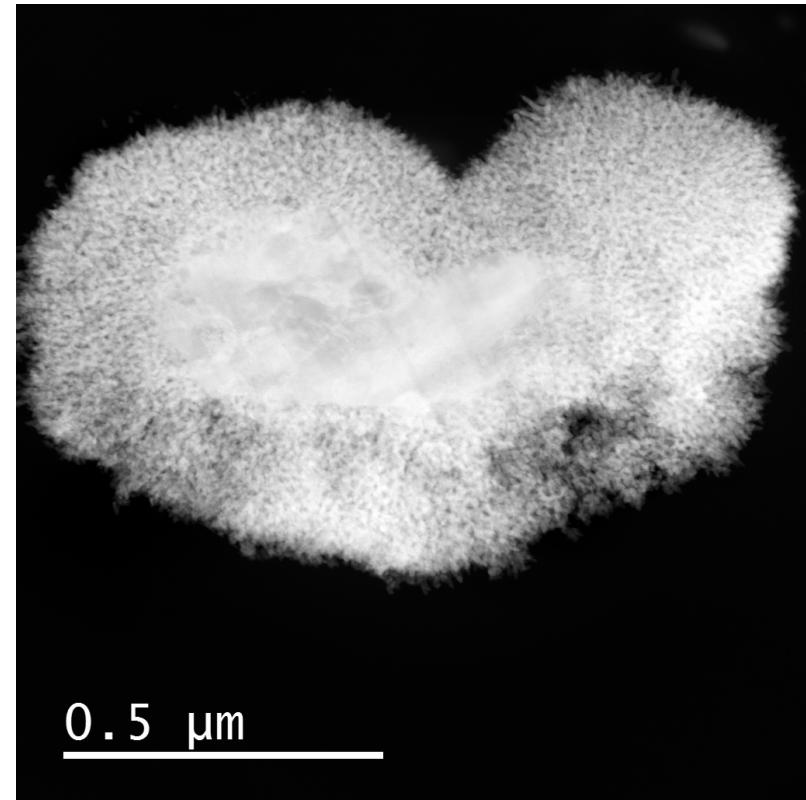
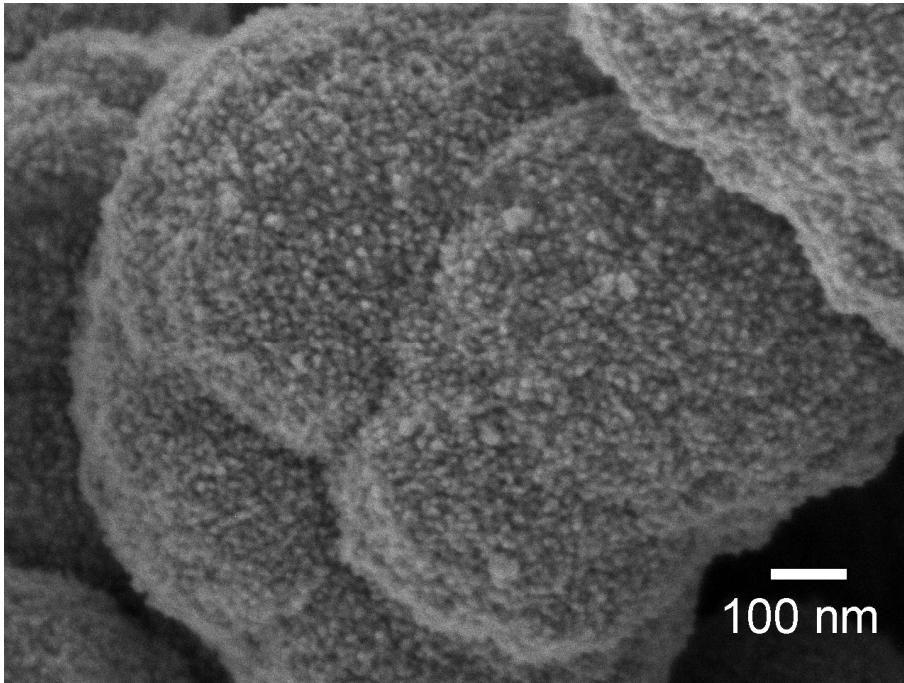


Pluronic F127 is $\text{EO}_{101}\text{PO}_{56}\text{EO}_{101}$
 $\text{EO}_2\text{PO}_2\text{EO}_2$ is :



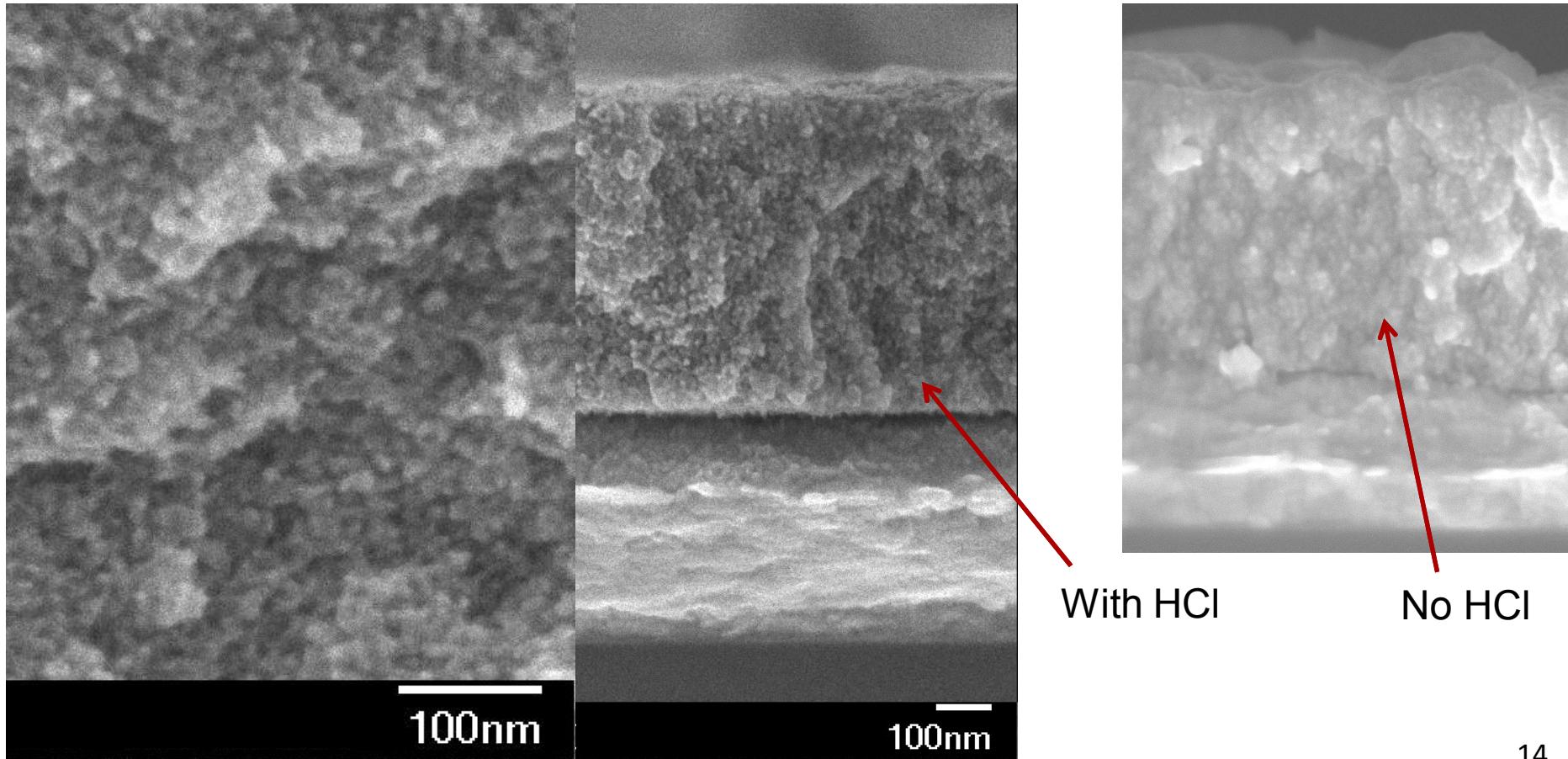
Iterative Electroless Porous Pd

- Stepwise growth of nanoporous Pd from dilute F127
 - $\text{Pd} + \text{H}_2 \rightarrow \text{PdH}_{0.6}$
 - $\text{PdH}_{0.6} + \text{Na}_2\text{PdCl}_4 + \text{F127} \rightarrow \text{porous Pd} + \text{HCl}$
- Films or powders



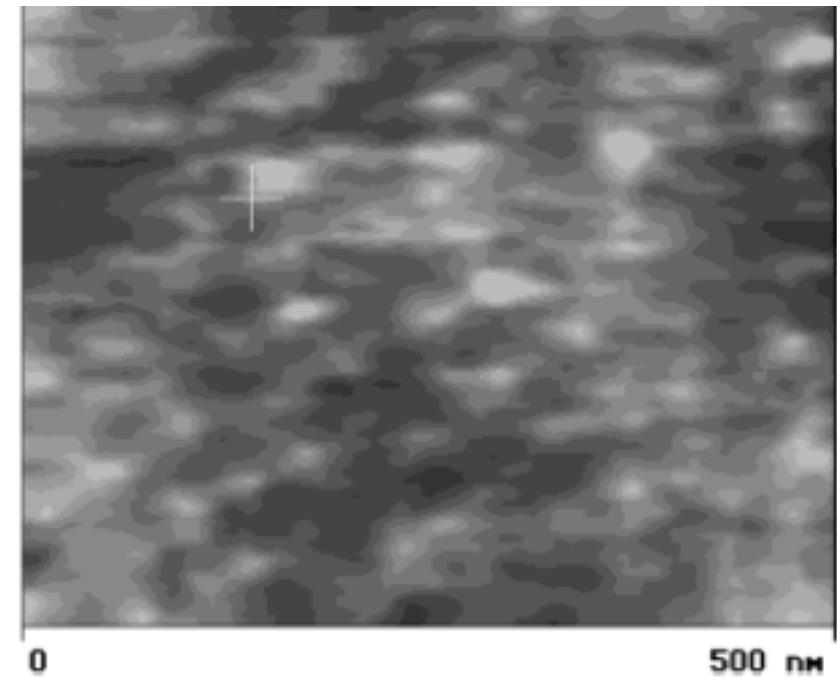
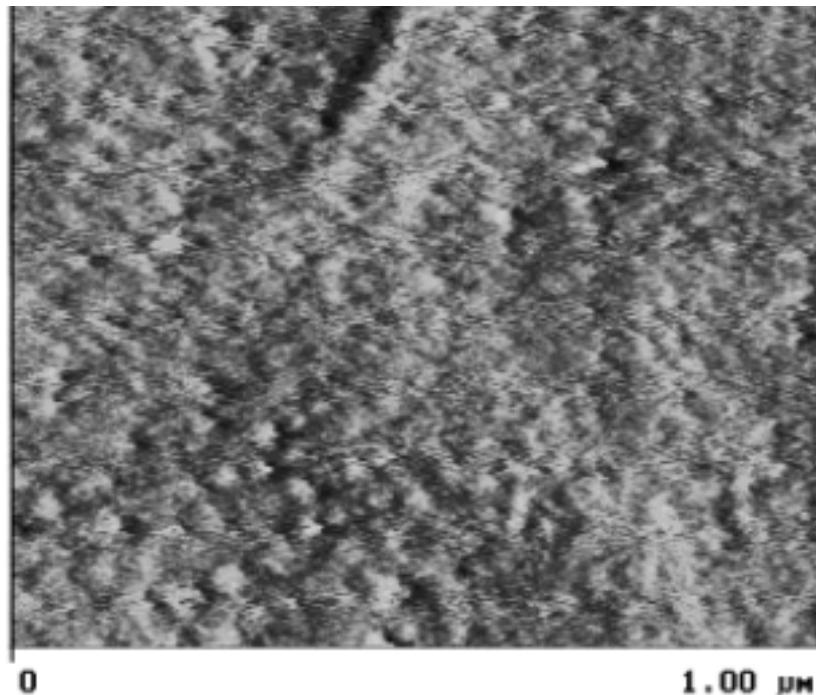
Growth rate is modest

- Growing too fast yields nanocrystalline, nonporous film
- Slow growth by stabilizing Pd^{2+} by Le Chatelier's principle
- Porosity quantified by electrochemical impedance measurements



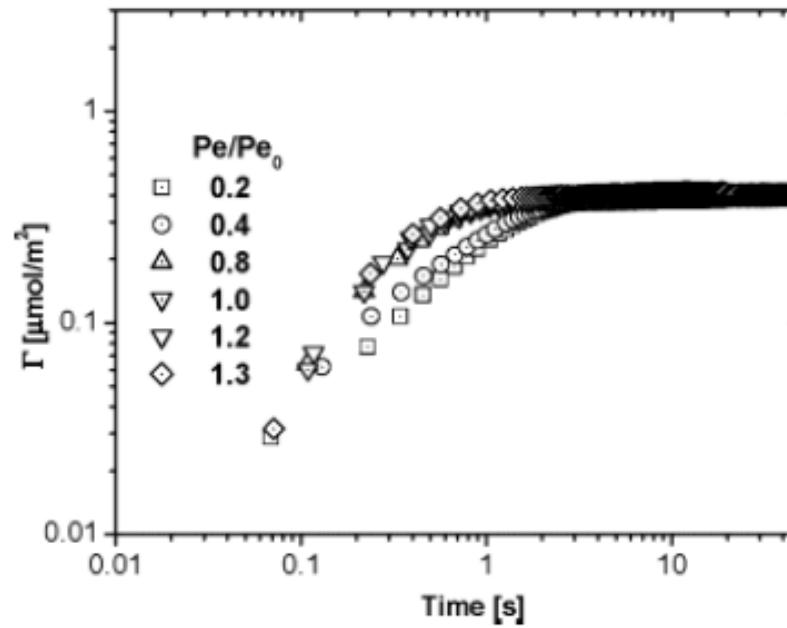
Surface assembly of micelles

- Brandani and Stroeve, Macromol. 36 9492 (2003)
- Liquid cell AFM of dilute $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ on $\text{C}_{11}\text{SH-Au}$



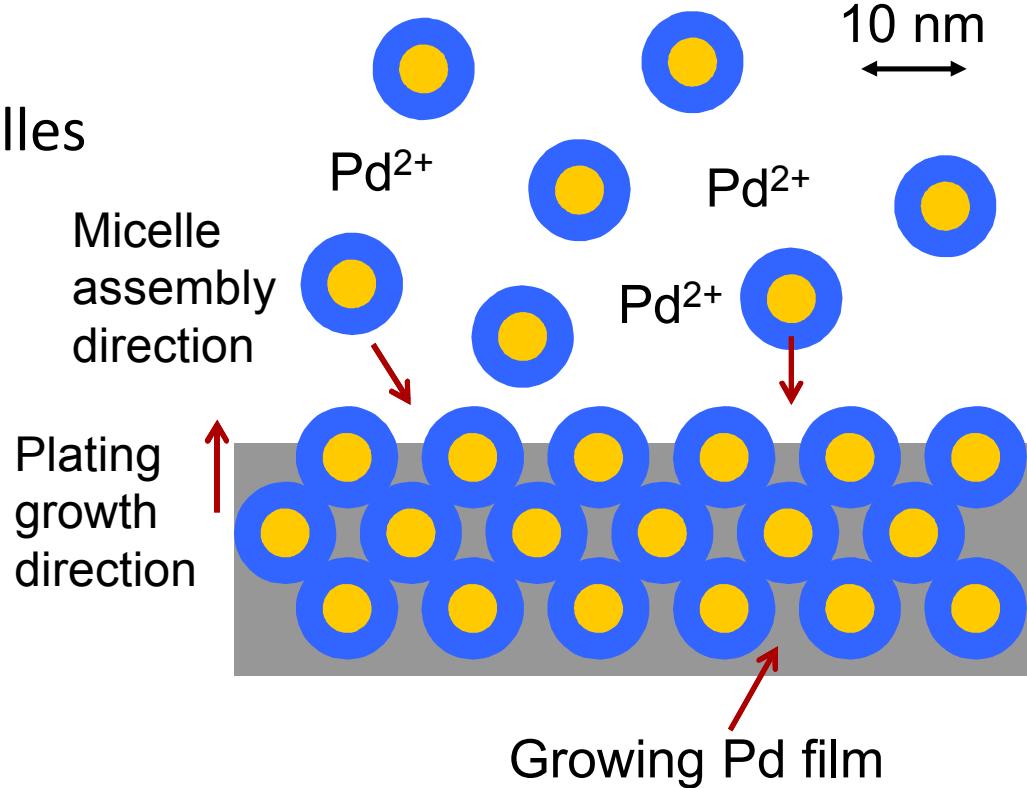
Assembly kinetics

- Brandani and Stroeve, Macromol. 36 9502 (2003)
- Surface plasmon resonance of 3 mM $\text{EO}_{37}\text{PO}_{56}\text{EO}_{37}$ on $\text{C}_{11}\text{SH-Au}$
- Adsorption timescale is around 1 s
- Flow rate-dependent



Plating growth mechanism

- Micelles adsorb to surface
- Growth occurs around micelles
- Repeat



- Chemical reduction: aggregation of seed particles around micelles
- Dilute electroplating: aggregation of micelles on growing surface

Summary

- Nanoporous metals can be obtained by metal growth around surfactant templates
- Bulk chemical reduction, electroless, or electrodeposition
- Concentrated or dilute surfactants
- Understanding of mechanism aids optimization, generalization, scale-up
 - Balance of:
 - Nucleation
 - Growth
 - Particle assembly
 - Micelle assembly
- Enabled by detailed characterization, compositional tunability

Acknowledgements

- Patrick J. Cappillino
- Christopher G. Jones
- Michelle A. Hekmaty
- Michael S. Kent
- Benjamin W. Jacobs
- Joshua D. Sugar
- Ryan K. Nishimoto
- Mark Homer
- George M. Buffleben
- Rex Hjelm (Los Alamos)
- Lucas R. Parent (Pacific Northwest National Laboratory)
- Ilke Arslan (Pacific Northwest National Laboratory)

