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Surfactant-Templated Nanoporous Metal Films and Powders

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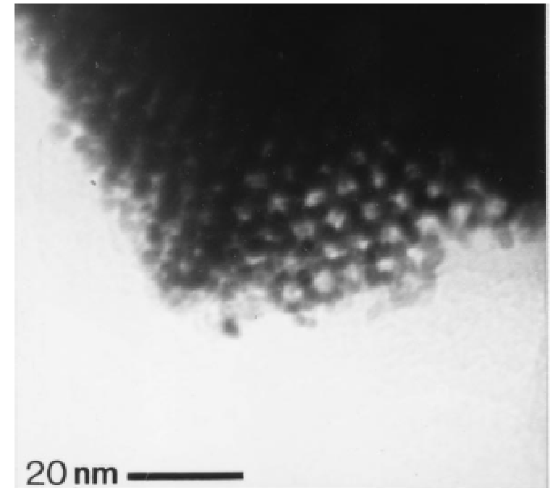
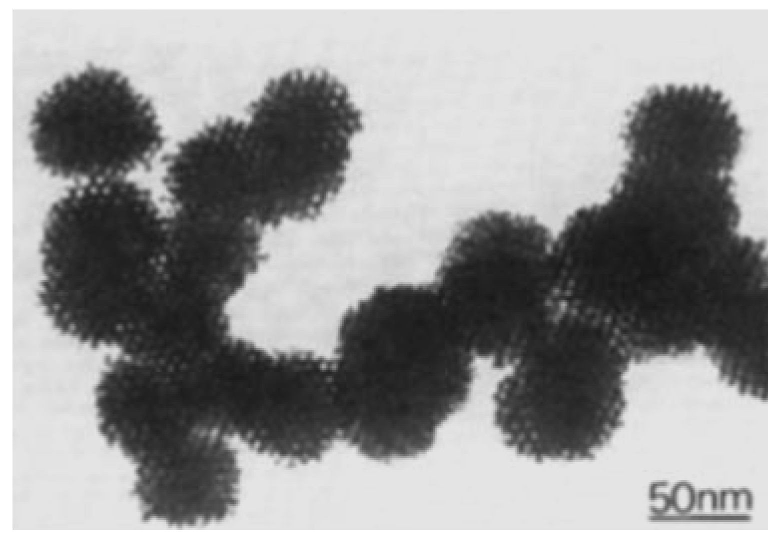
Early templated porous metals

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



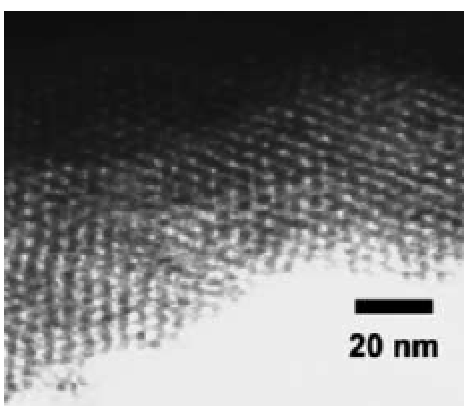
- Attard et al.,
  Angew. Chem. 36 1315 (1997)
- N_2H_4-reduced Pt particles →

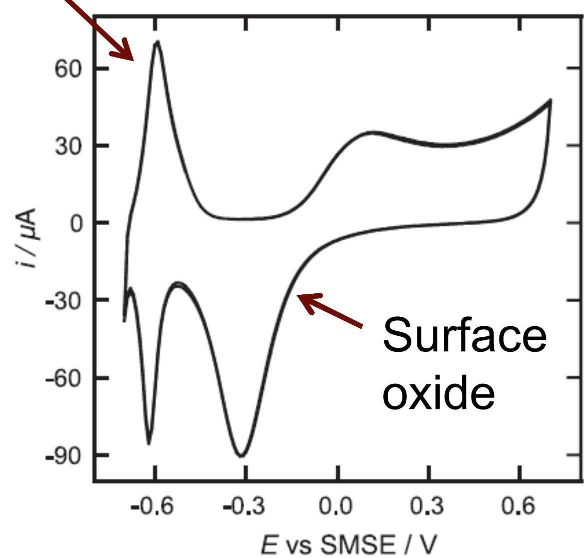


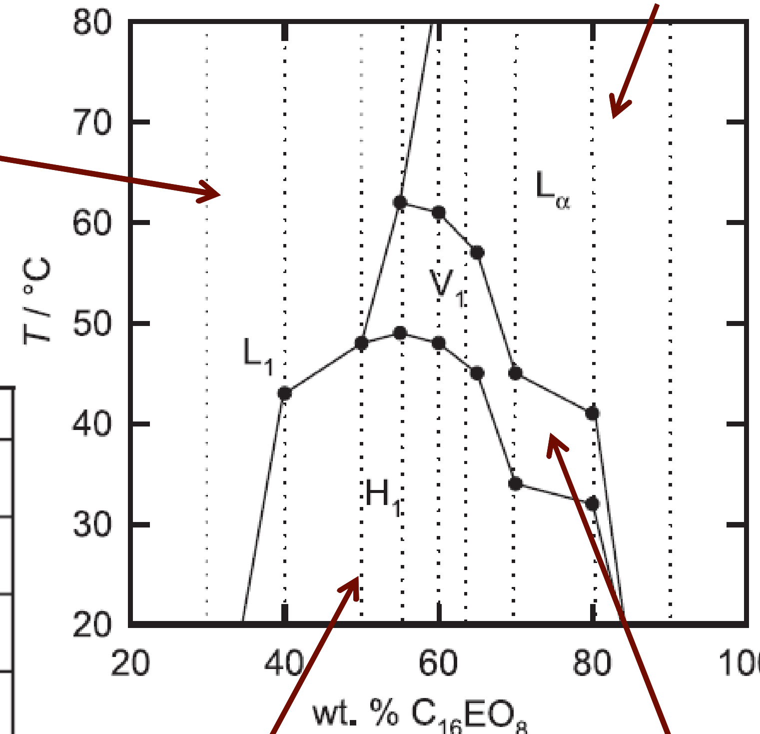
$C_{10}EO_2$ surfactant:

Plating in lyotropic liquid crystals

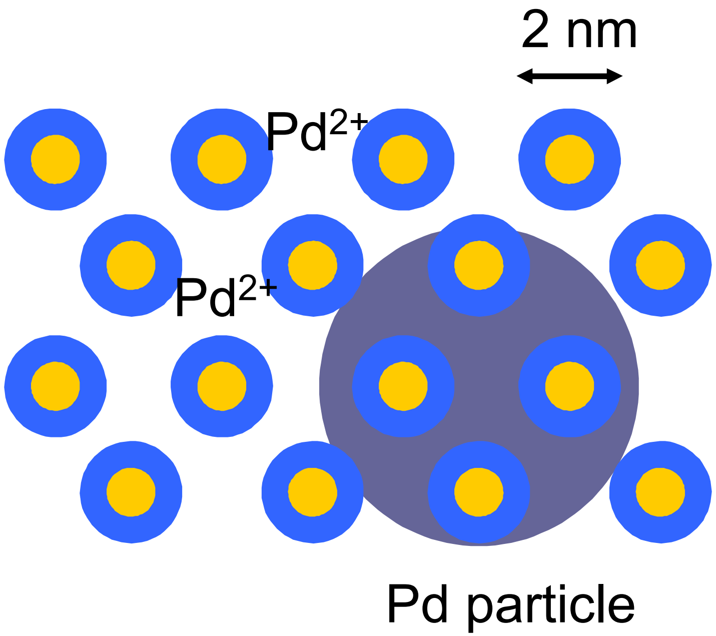
- Bartlett and Marwan,
  Microporous Mesoporous Mater 62 73 (2003)
- Heptane swelling agent
- Electroplated Rh
- 30 m^2/g



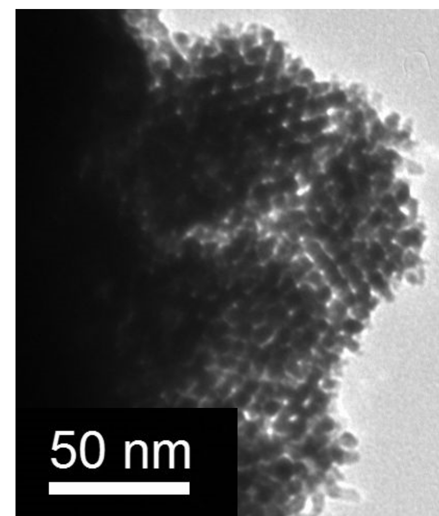




Reduction in lyotropic liquid crystals



$(NH_4)_2\ PdCl_4 + H_2 \rightarrow Pd + 2\ NH_4Cl + 2HCl$



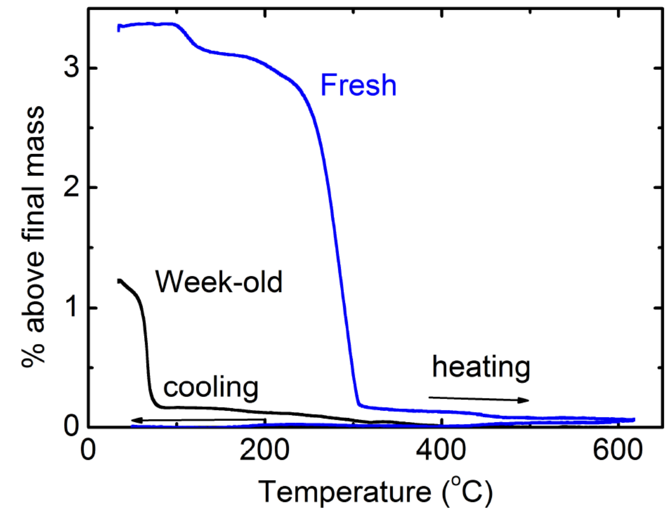
- Robinson et al.,
  Int. J. Hydrogen Energy 35 5423 (2010)
- Particles grow around surfactant phase
- Pd and PdRh alloys

Surfactant removal

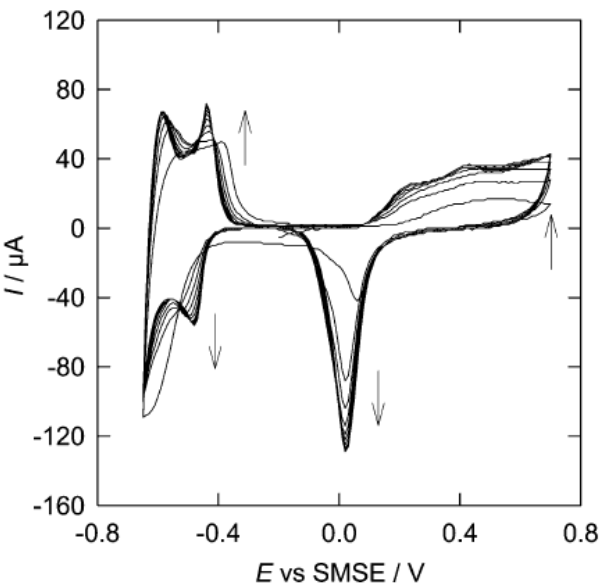
- Can require long soaks

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

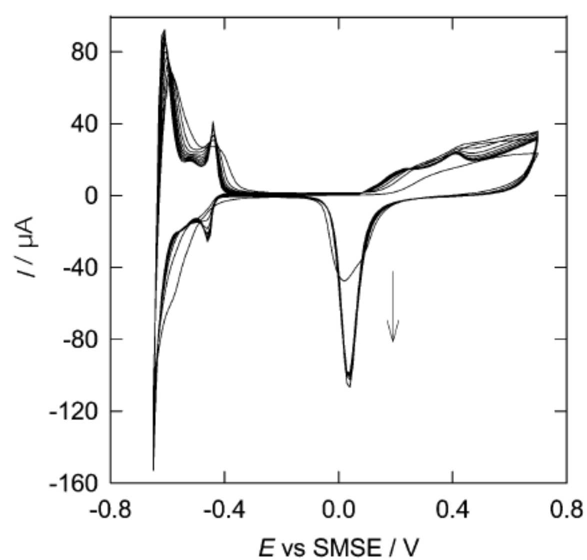
200 nm Pd film from Brij 56 (impure $C_{16}EO_8$)
- Surfactant residue impacts electrochemical kinetics



10 min water soak



60 min water soak



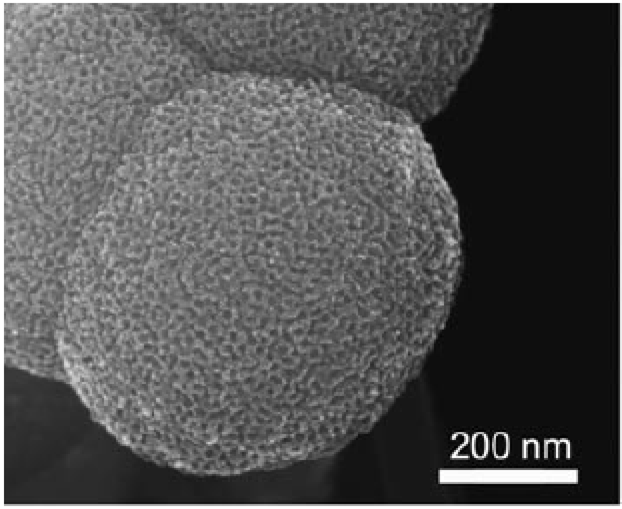
- Easier with oxidized surfaces

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

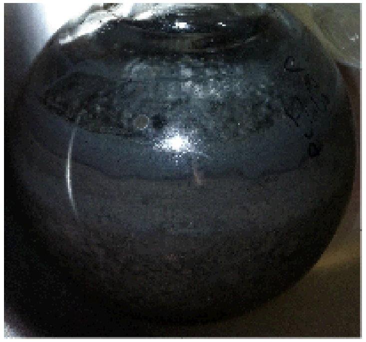
Pd:Rh 9:1
4h ethanol-water soak

Block copolymer gels

- Pt films from Block copolymer gels
  Yamauchi et al., Angew. Chem. 47 5371 (2008)
  Takai et al., JACS 132 209 (2010)
- Pores in SEM range

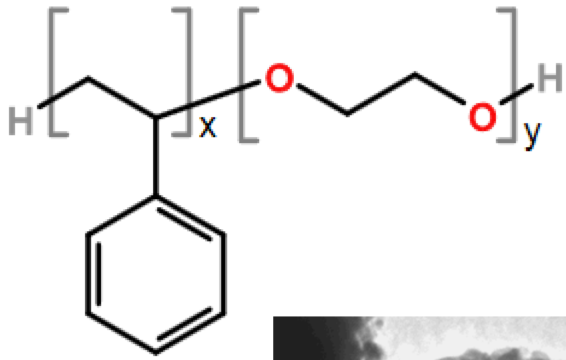


- Gram scale, H_2-reduced Pd
  Cappillino et al.
  J. Mater. Chem. A 1 602 (2013)

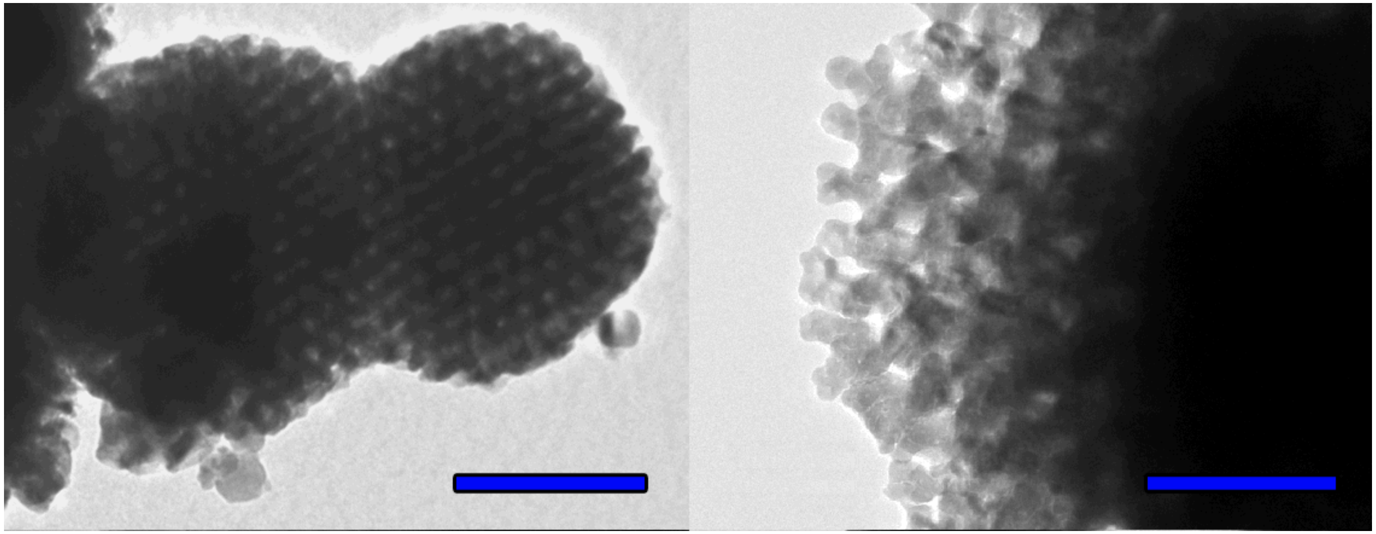


Size tuning with block copolymers

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



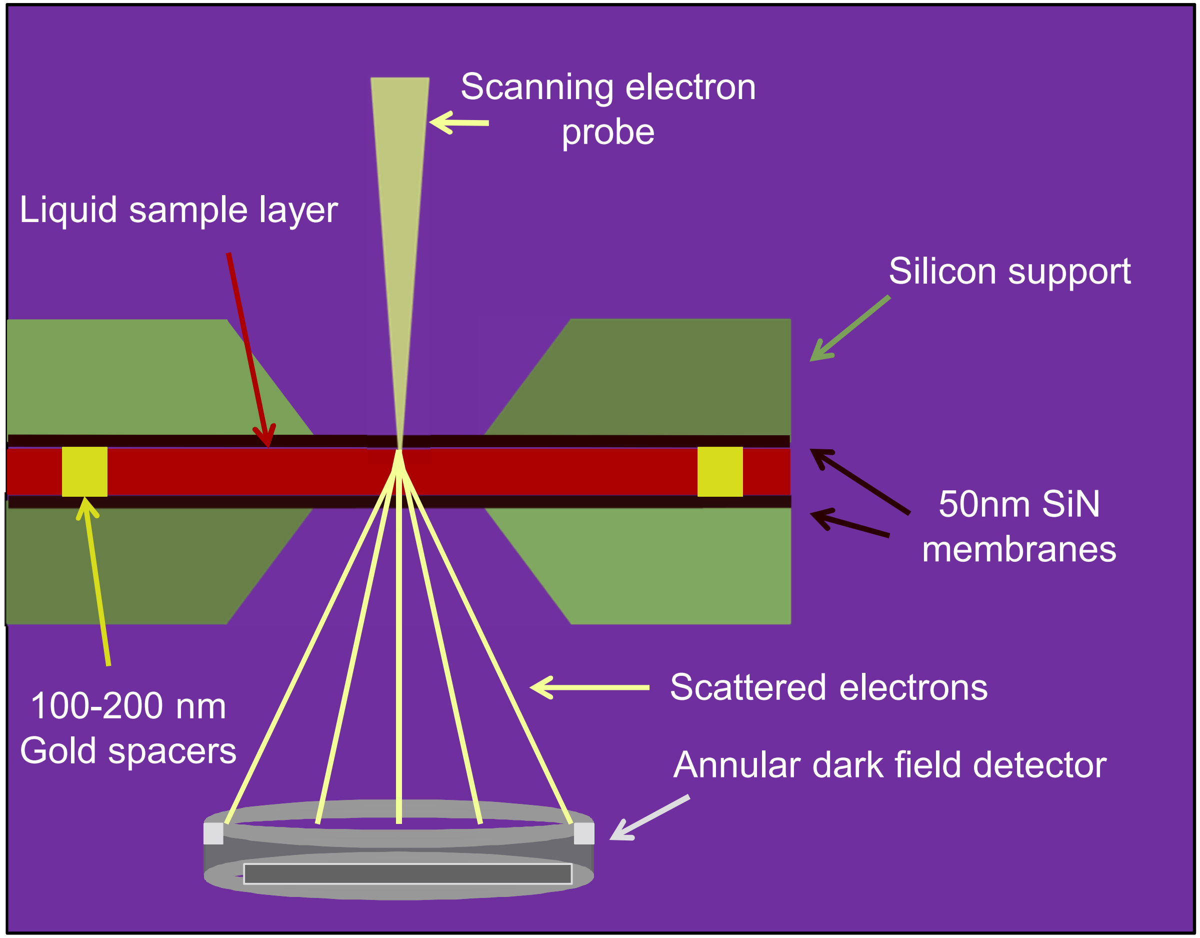
Name	x	y	Pore, nm	Pitch, nm
Pd_S	22	70	7	15
Pd_L	36	113	12	30



100 nm 100 nm

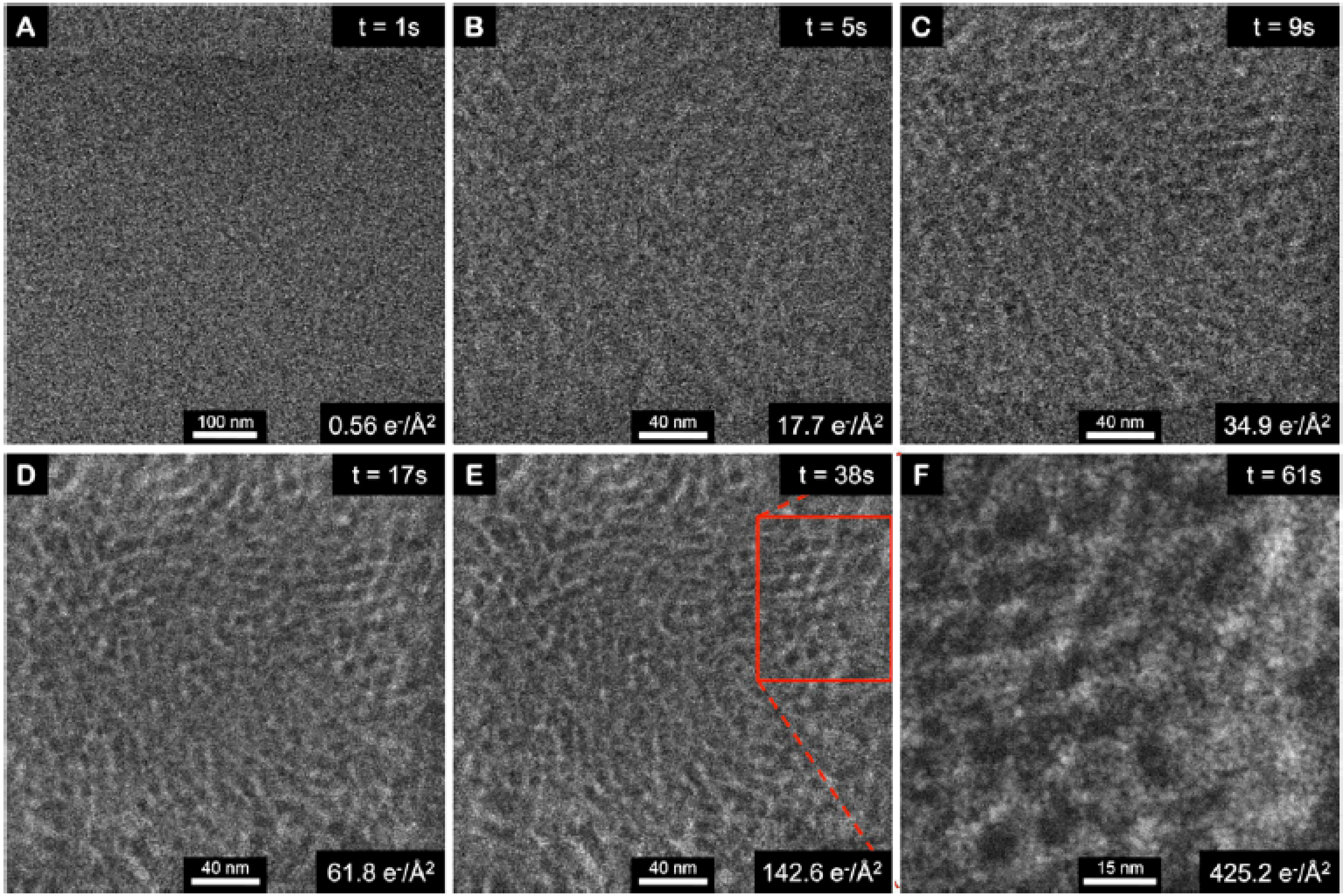
Liquid cell electron microscopy

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



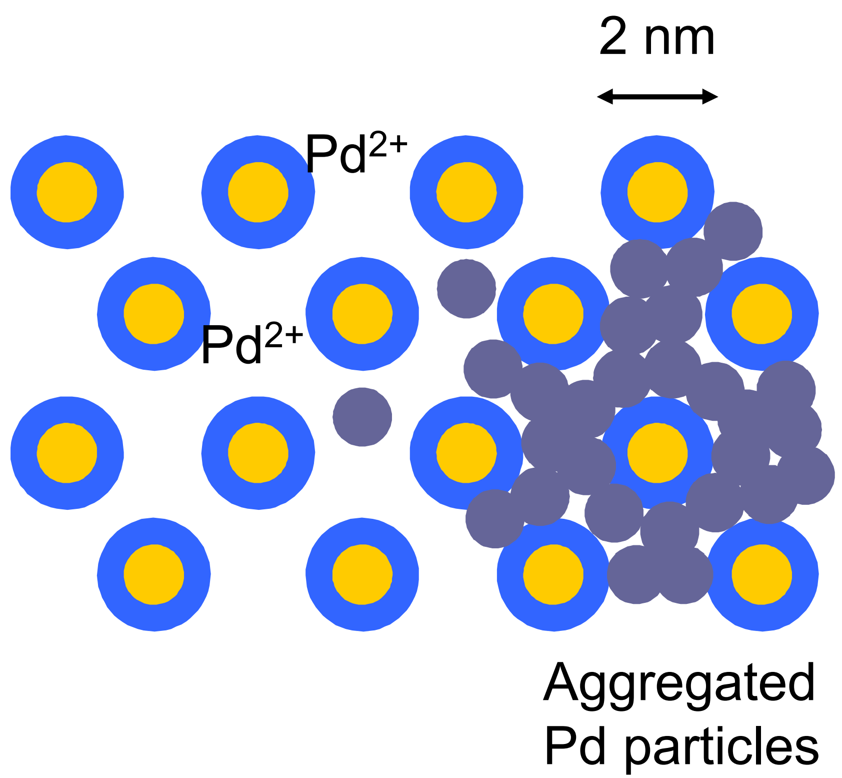
Liquid cell electron microscopy

- Bulk reduction: nucleation, aggregation, sintering

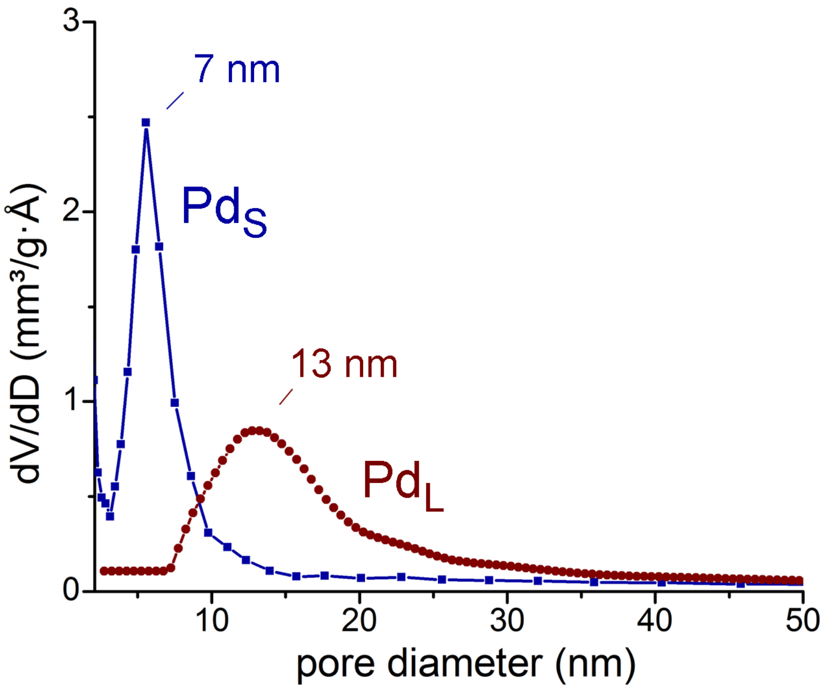


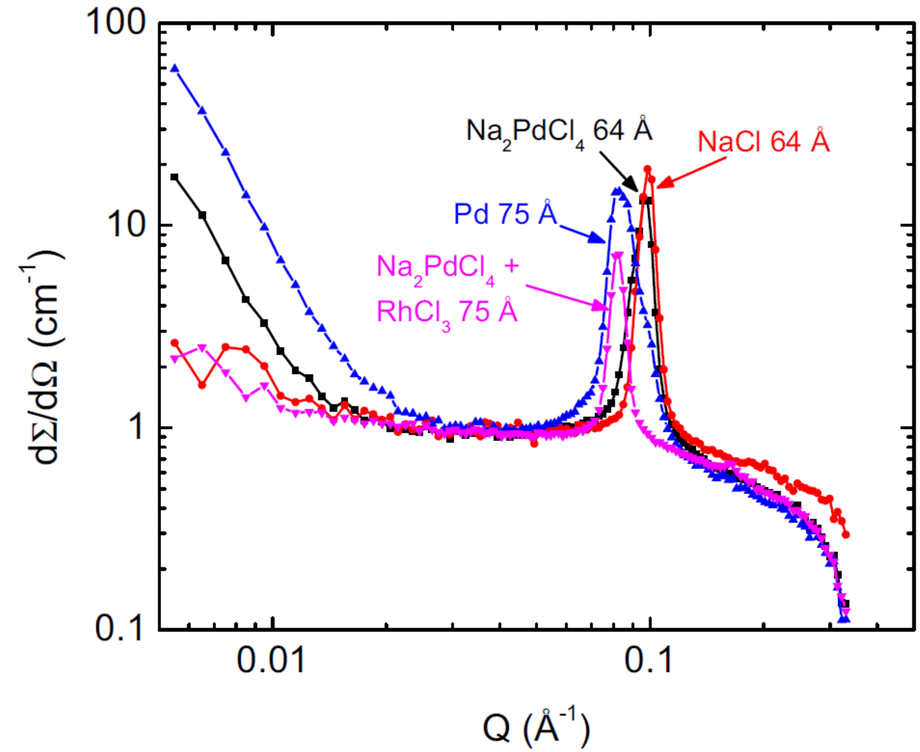
Chemical reduction: mechanism

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



Bulk measurements corroborate EM



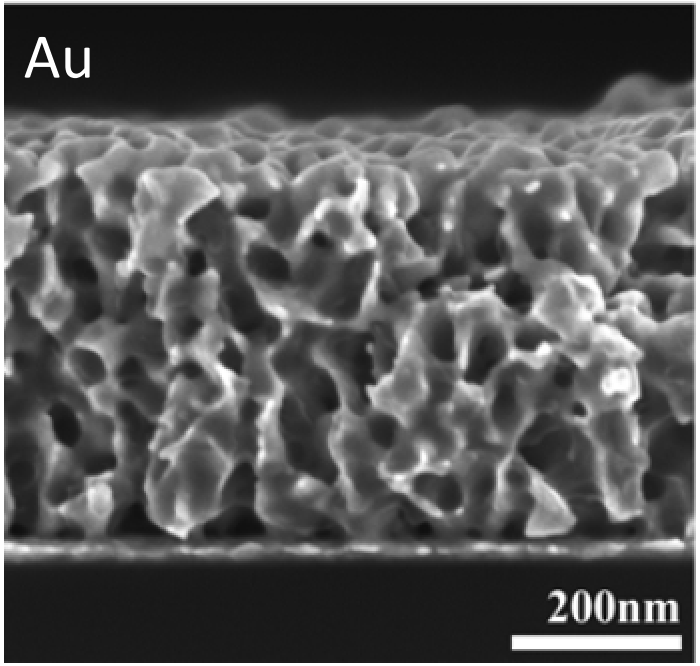


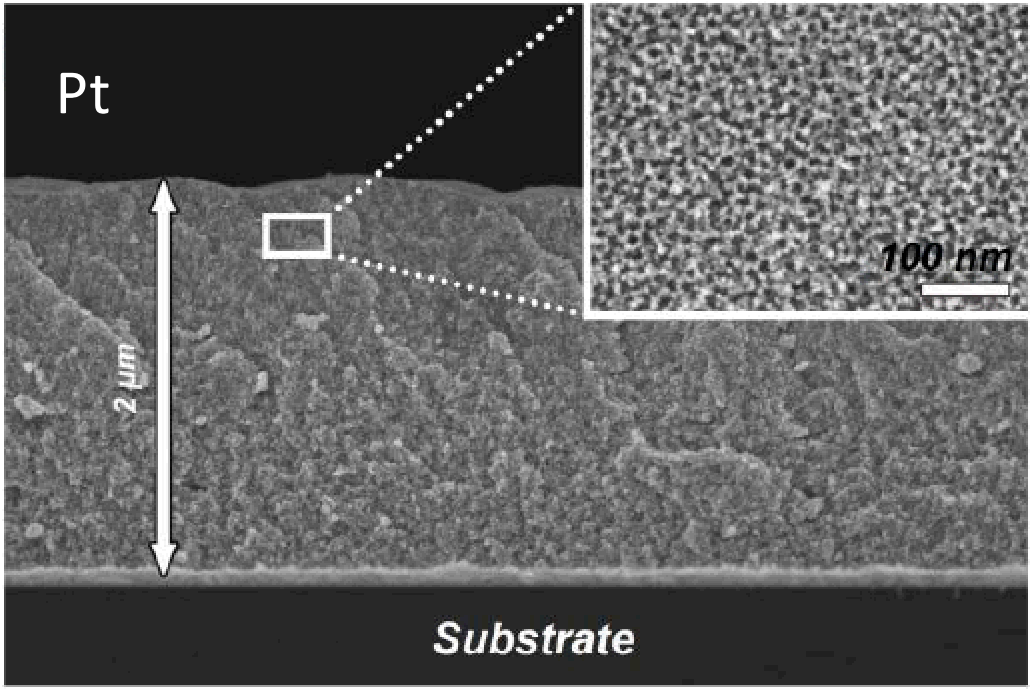
N_2 porosimetry shows pore size
PS-PEO block copolymer
J. Mater. Chem. A 1 603

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

Plating from dilute micellar phase

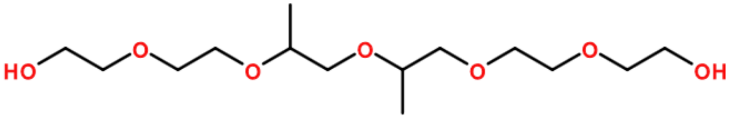
- Eliminates slow, messy pastes, gels; pores less ordered
- Pt + F127: Wang et al., Chem. Mater. 24 1591 (2012)
- Au + PS-PEO: Li et al., Nature Comm. 6 6608 (2015)
  - Uses mixed solvent





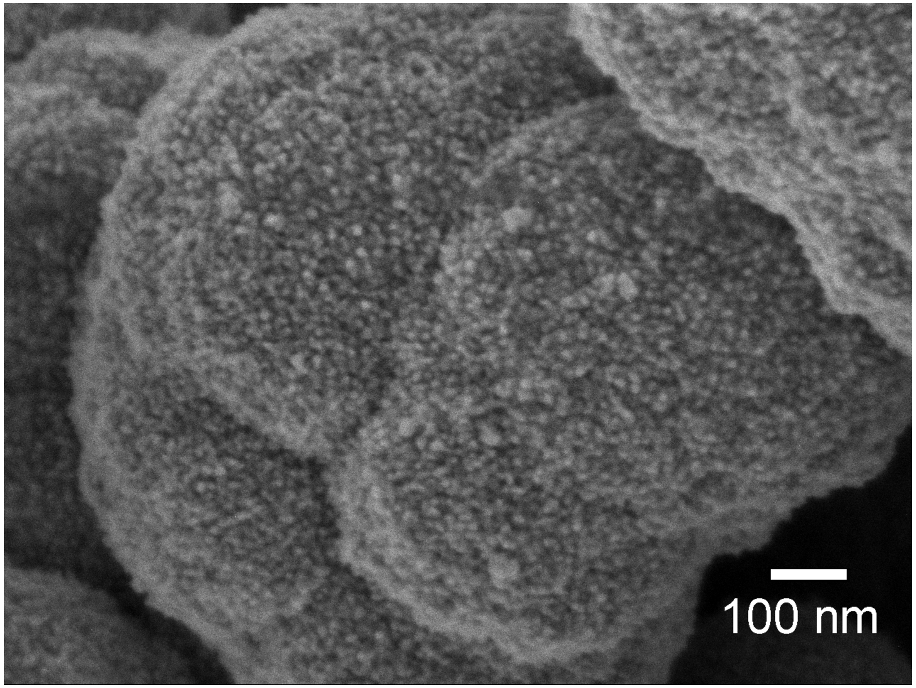
Pluronic F127 is EO_{101} PO_{56} EO_{101}

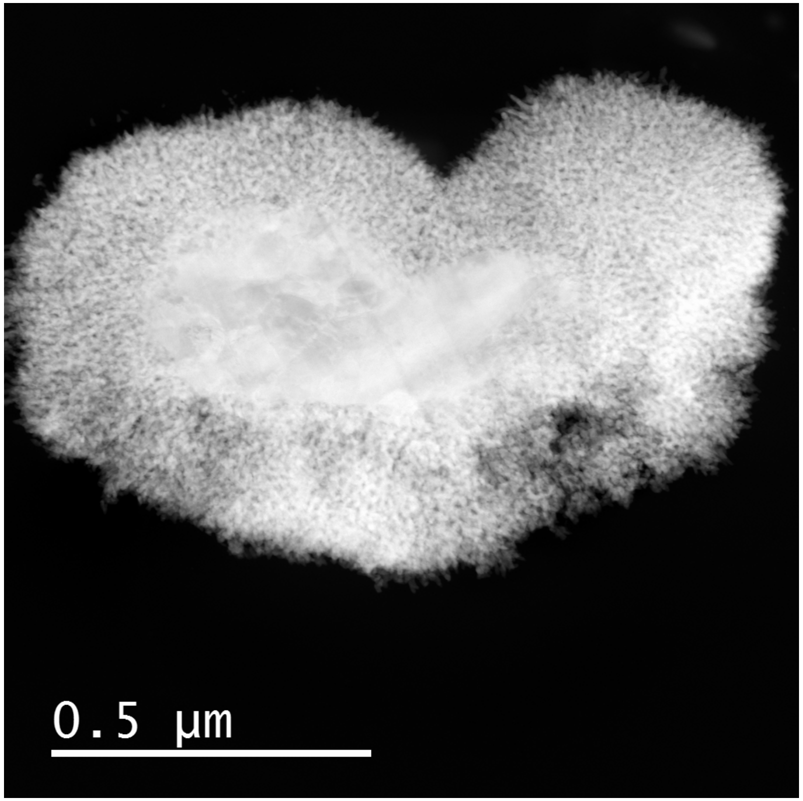
$EO_2PO_2EO_2$ is :



Iterative Electroless Porous Pd

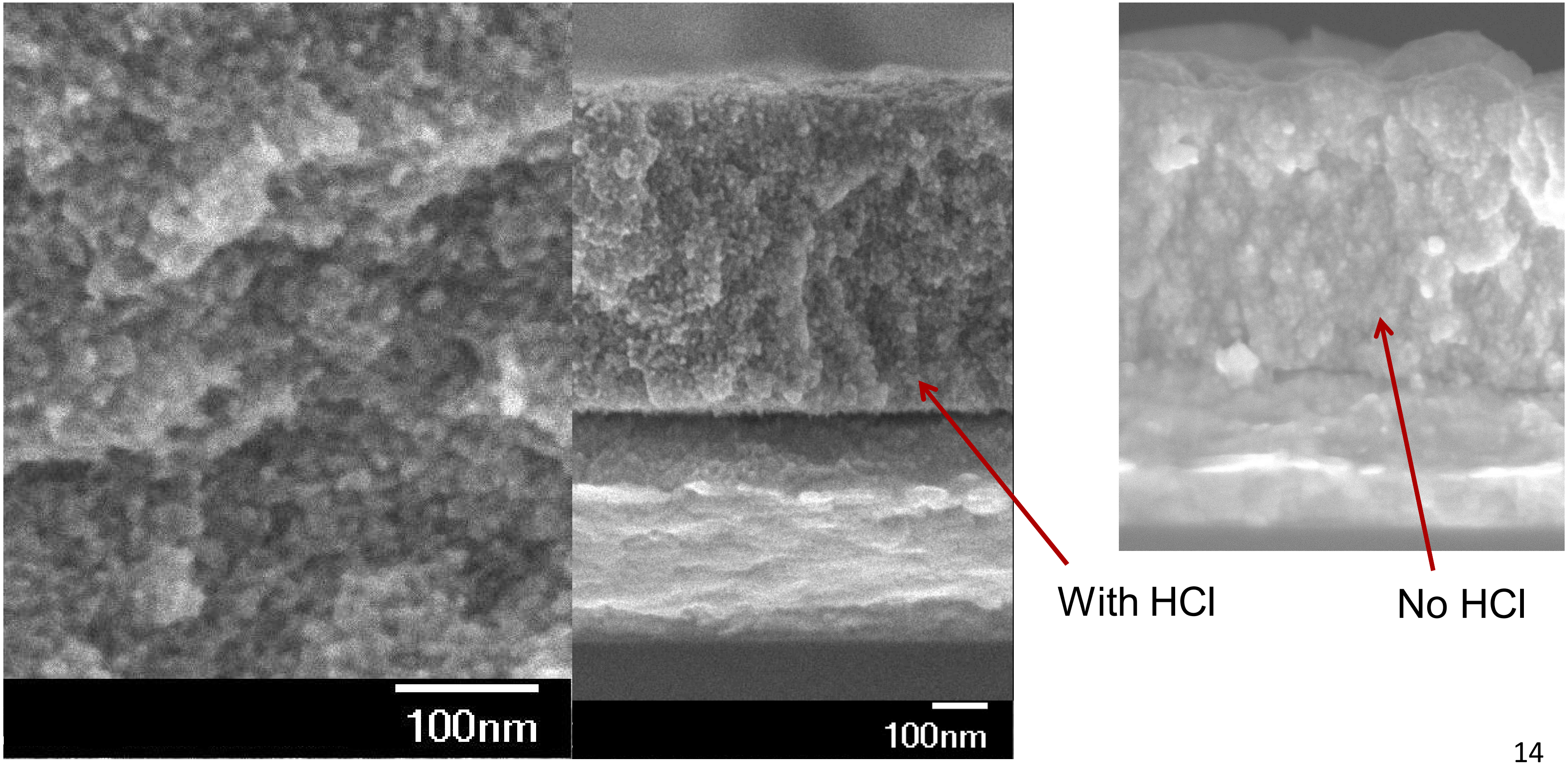
- Stepwise growth of nanoporous Pd from dilute F127
  - $Pd + H_2 \rightarrow PdH_{0.6}$
  - $PdH_{0.6} + Na_2PdCl_4 + F127 \rightarrow$ porous Pd + HCl
- Films or powders





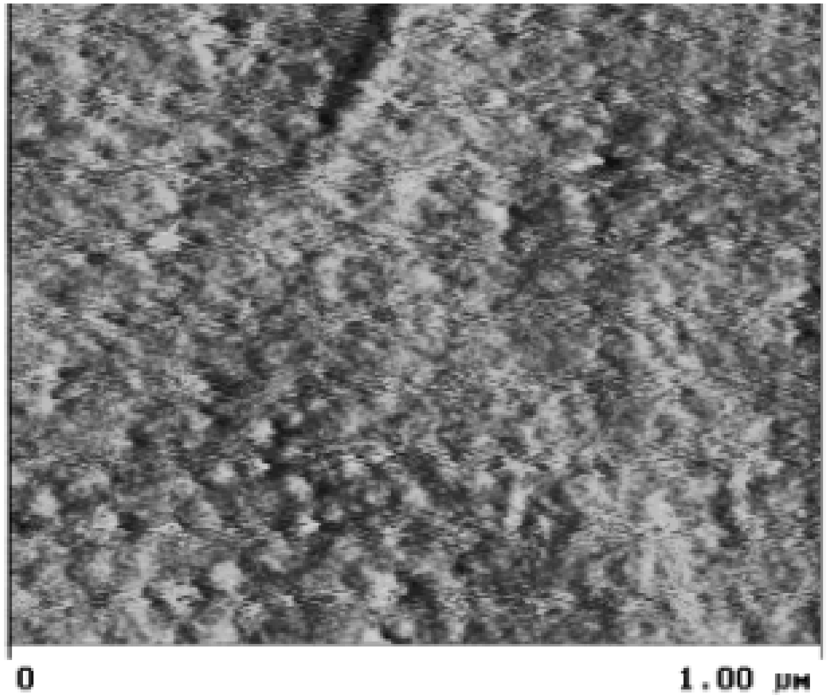
Growth rate is modest

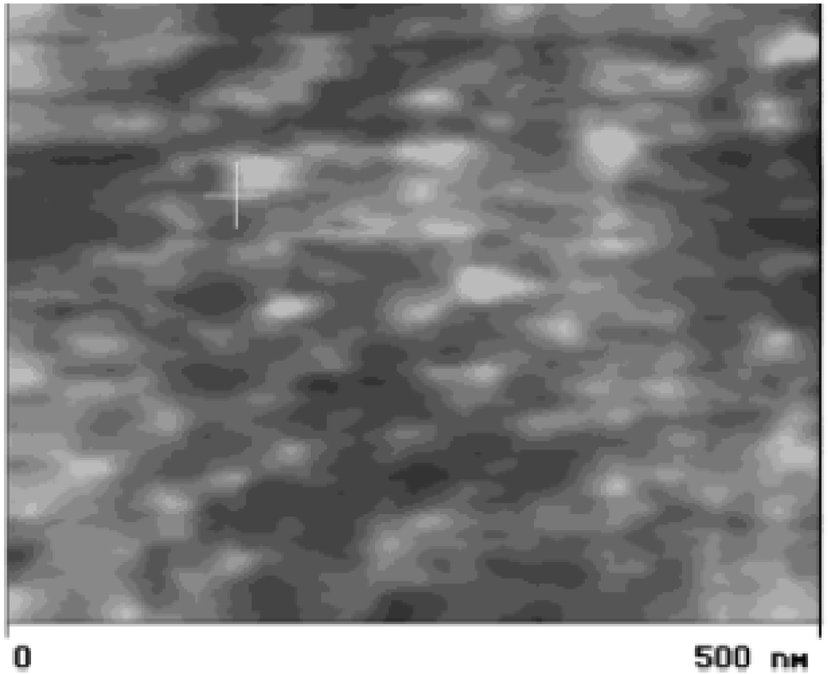
- Growing too fast yields nanocrystalline, nonporous film
- Slow growth by stabilizing Pd^{2+} by Le Chatelier's principle
- Porosity quantified by electrochemical impedance measurements



Surface assembly of micelles

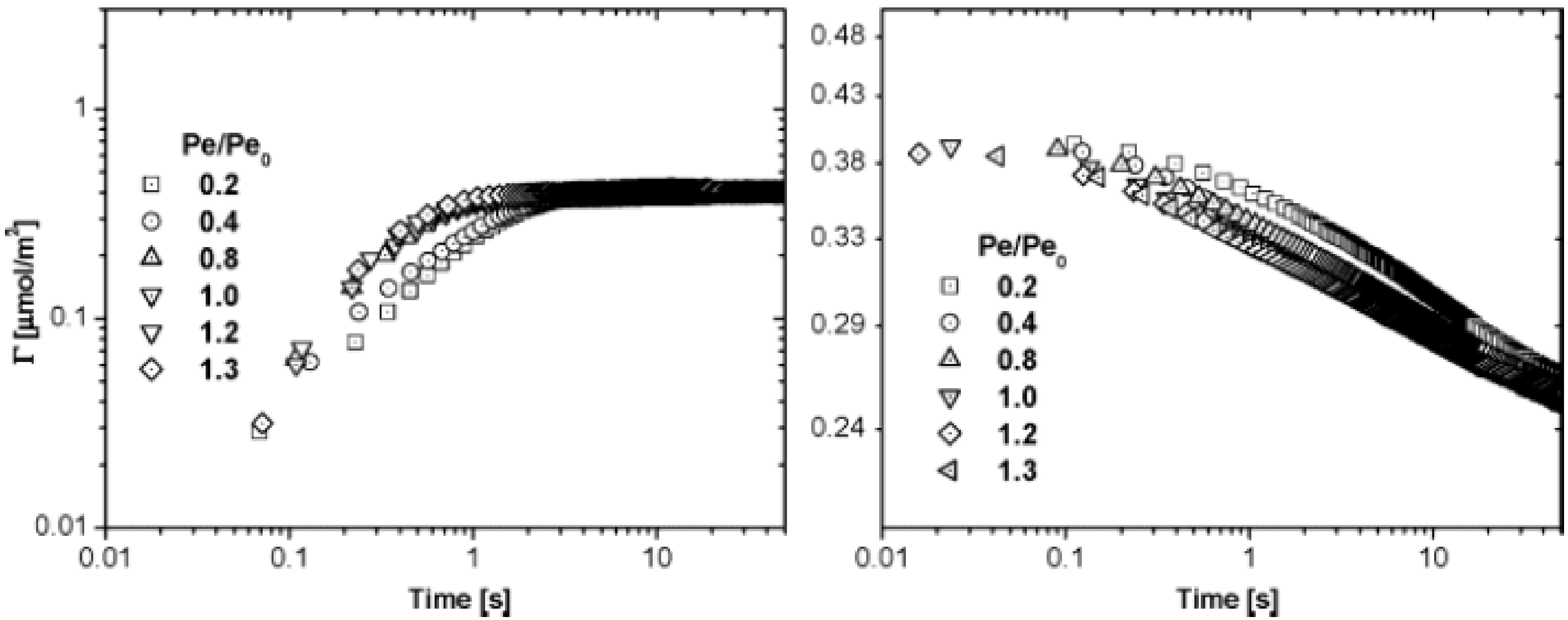
- Brandani and Stroeve, Macromol. 36 9492 (2003)
- Liquid cell AFM of dilute $EO_{37}PO_{56}EO_{37}$ on $C_{11}SH$-Au





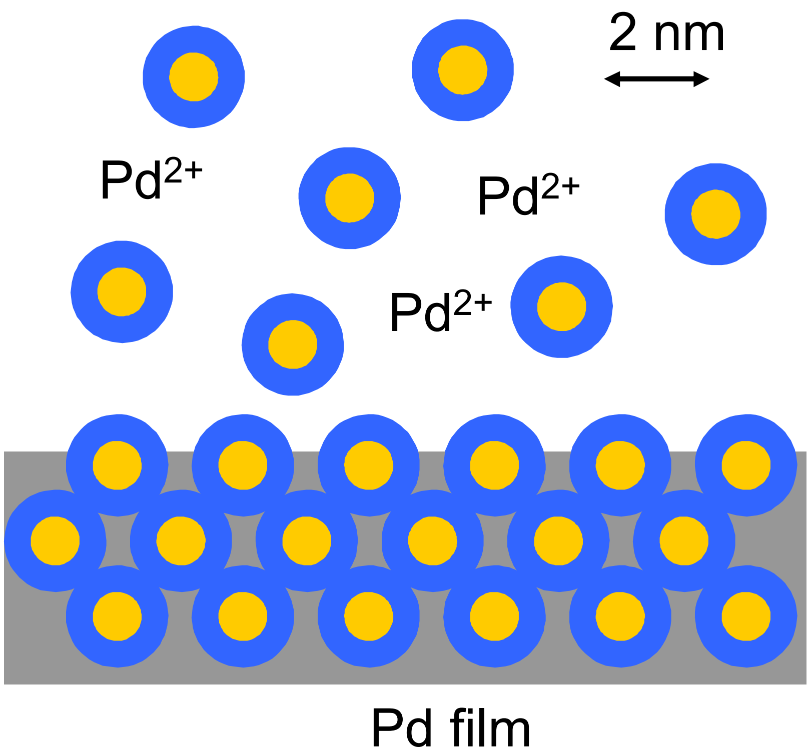
Assembly kinetics

- Brandani and Stroeve, Macromol. 36 9502 (2003)
- Surface plasmon resonance of 3 mM $EO_{37}PO_{56}EO_{37}$ on $C_{11}SH$-Au
- Adsorption/desorption timescale 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

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