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# Additive Manufacturing of Porous Materials

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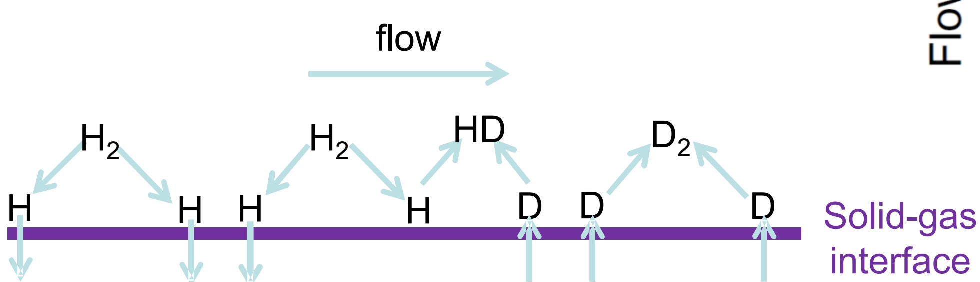
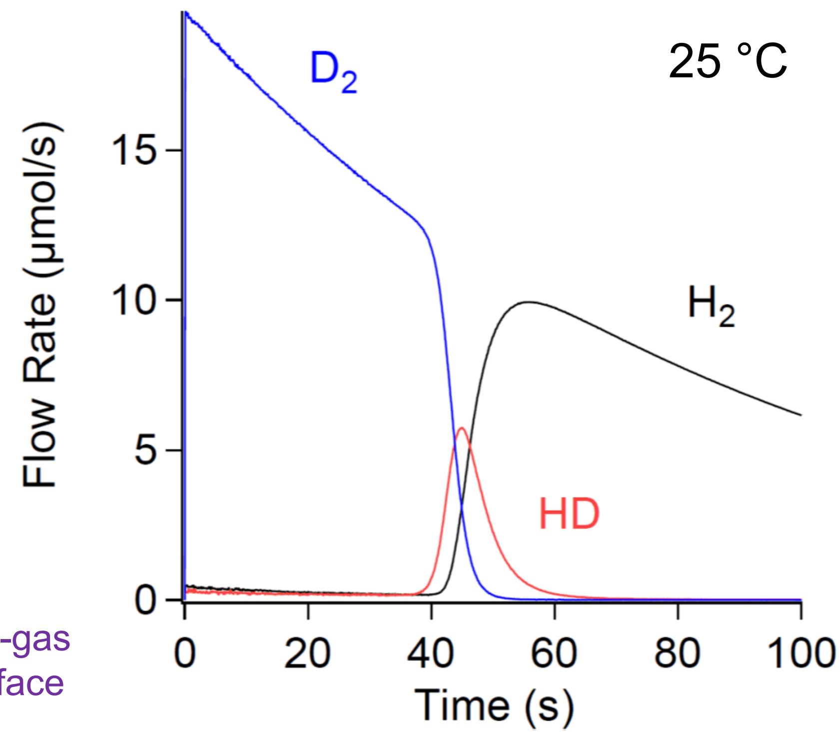
# 3D printing for chemical engineers

- Chemical engineers often rely on randomly packed (or sintered) powders
  - Catalyst and separation columns
  - Battery and fuel cell electrodes
  - Filters and separator membranes
- Optimized geometries can yield major performance and efficiency improvements
  - Capillary gas chromatography
  - Microfluidic medical devices
  - “3D” batteries with microfabricated electrodes
- Optimized geometries are difficult to build by conventional methods
- Our goal is to design, build, and test 3D-printed structures that demonstrate performance improvements for chromatography columns
- Key challenge: need macroscopic parts with microscopic features for good fluid-solid contact

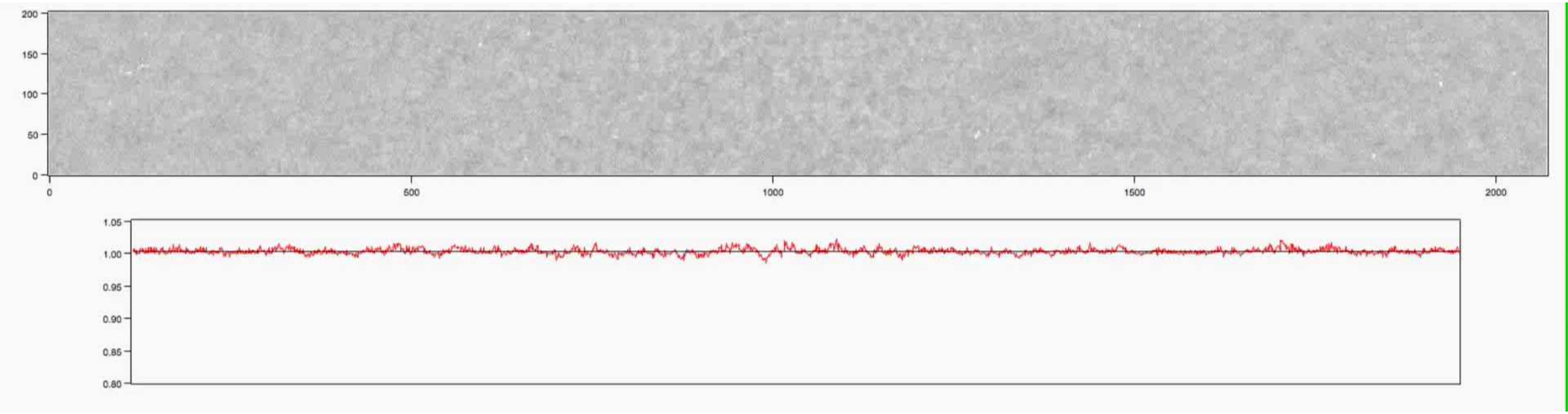
# Isotope exchange gas chromatography

- Second-order kinetics: sharp, steady-state composition boundary
- $H_2 + PdD_{0.6} \rightarrow D_2 + PdH_{0.6}$
- Elute with $H_2$ (protium), measure $D_2$ eluate with mass spectrometer
- HD peak width indicates broadening mechanisms
  - Reaction kinetics
  - Gas-phase axial, radial diffusion
  - Solid-phase diffusion (no bulk reaction)
- 2 mm diameter, 20 mm long column
- 190 mg Pd powder, 50 psi drop



# Neutron Imaging of Powder Column

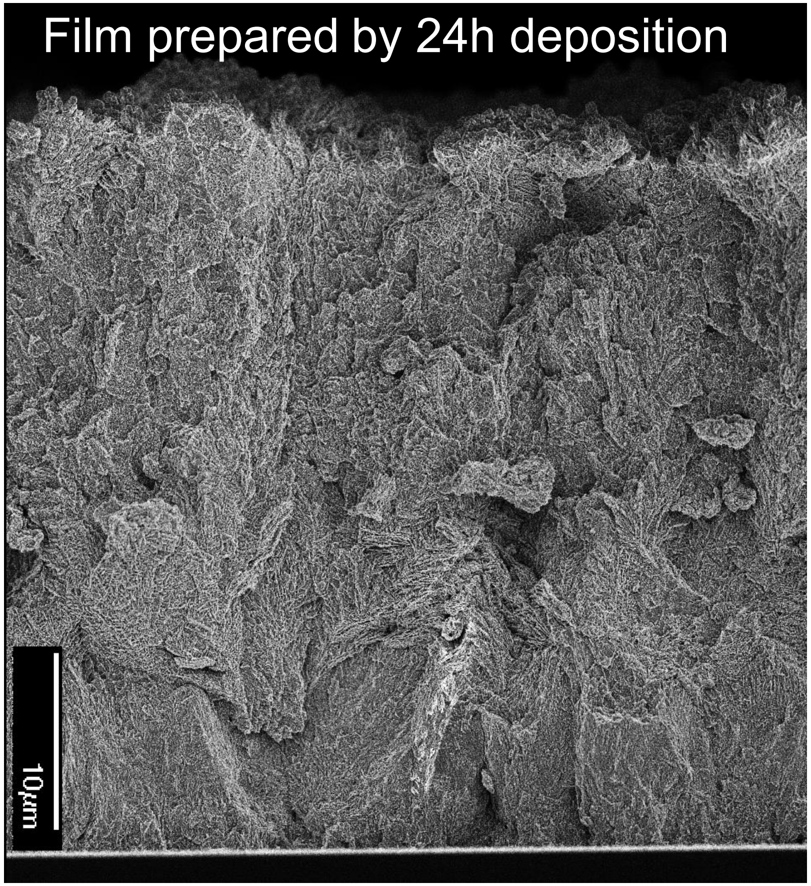


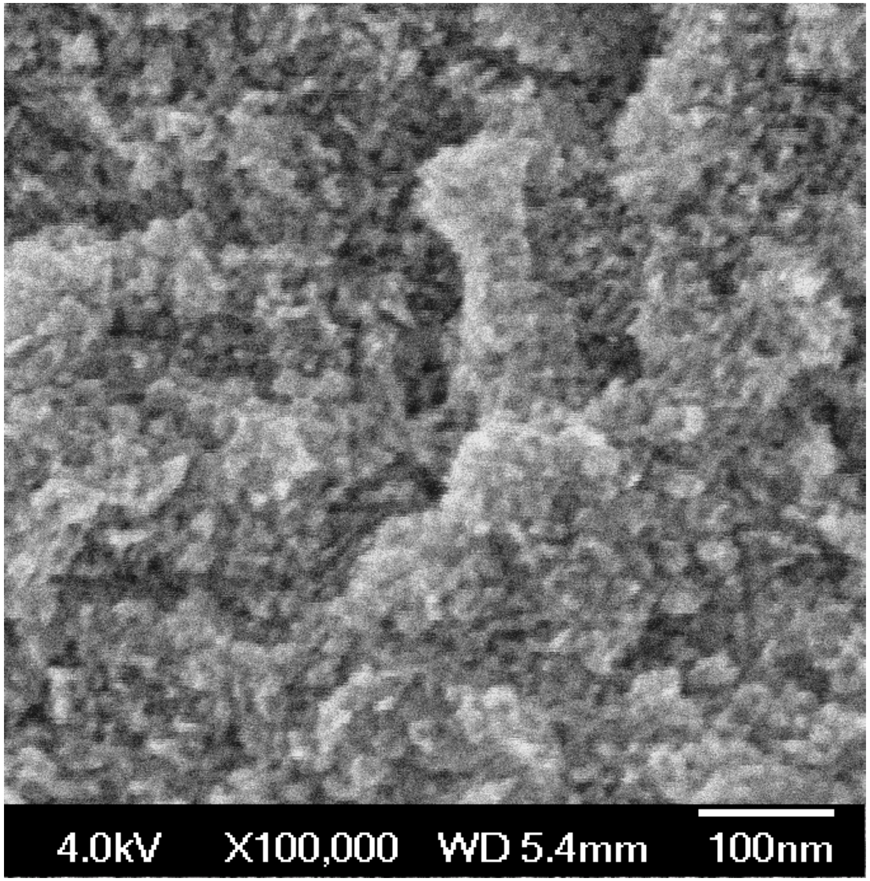

- 4x4x104mm column, square cross section
- Images are in millimeters, and movie is shown at 20x speed
- Plot (red) shows median transmittance of vertical pixels across column
- Black line is fit of error function (integral of Gaussian) to plotted data
- Hydride scatters neutrons and appears darker than the deuteride

We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron research facilities used in this work. Collaborators include David Jacobson, Daniel Hussey, and Eli Baltic.

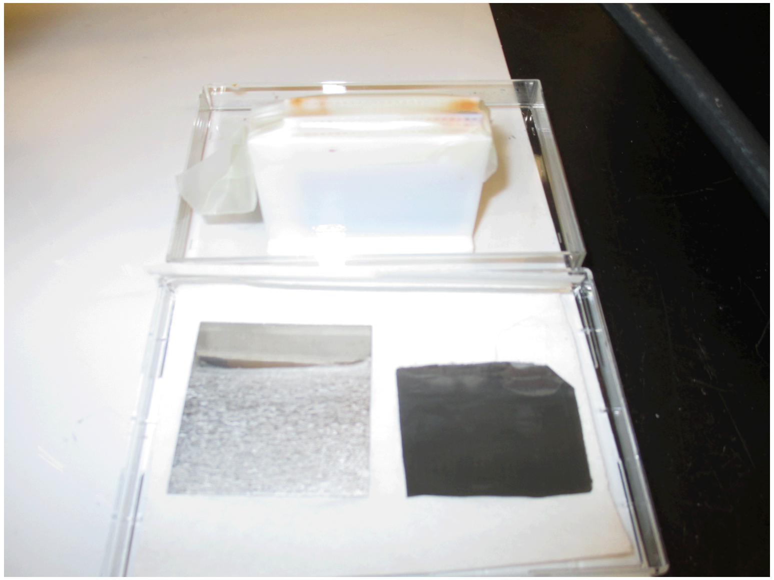
# Nanoporous Palladium Films

- Films prepared by electrodeposition with block copolymer pore template
- Disordered 10-20nm pores

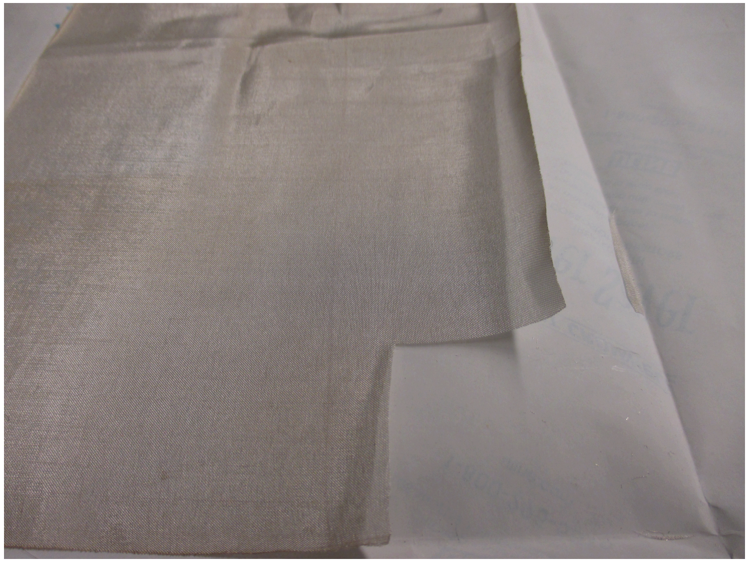


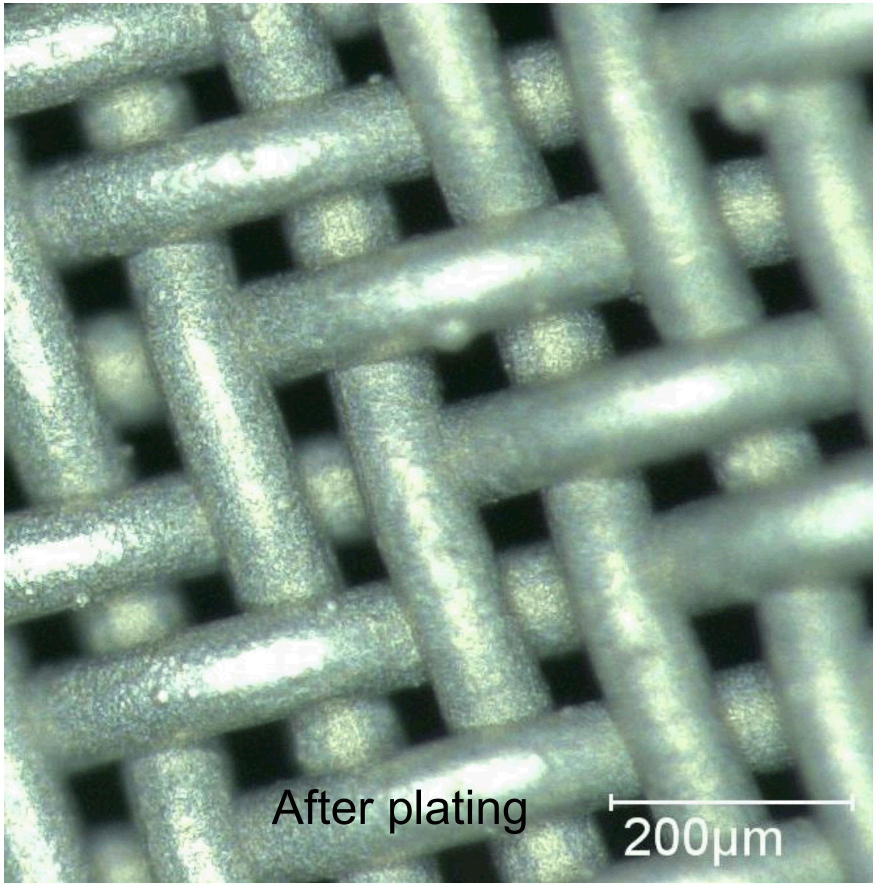



# Mesh plating for pore hierarchy



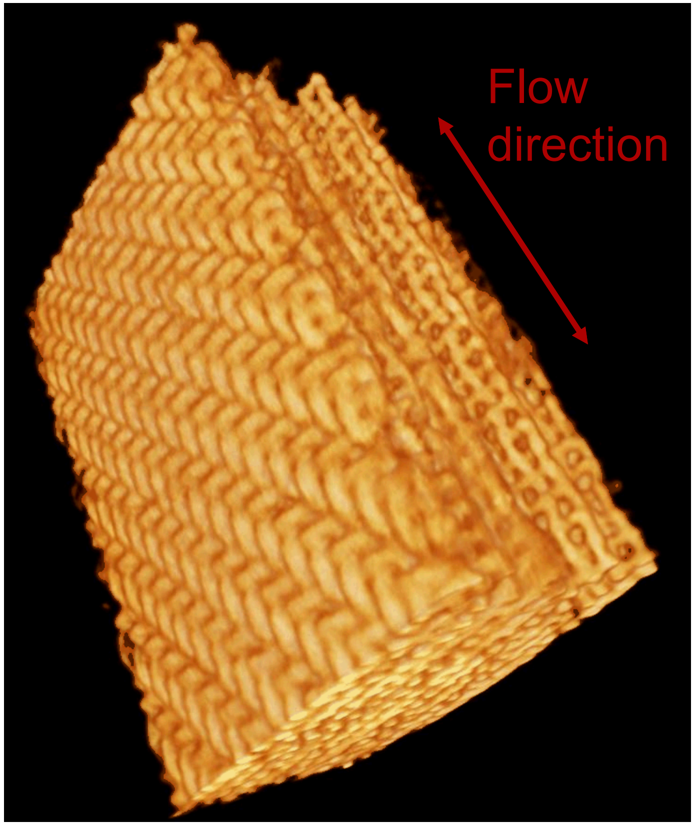
- 3D printed cell to optimize geometry
- 99.99% Pd anode plates 50x50x1mm
- Ag mesh: 50 µm wire, 127 µm pitch

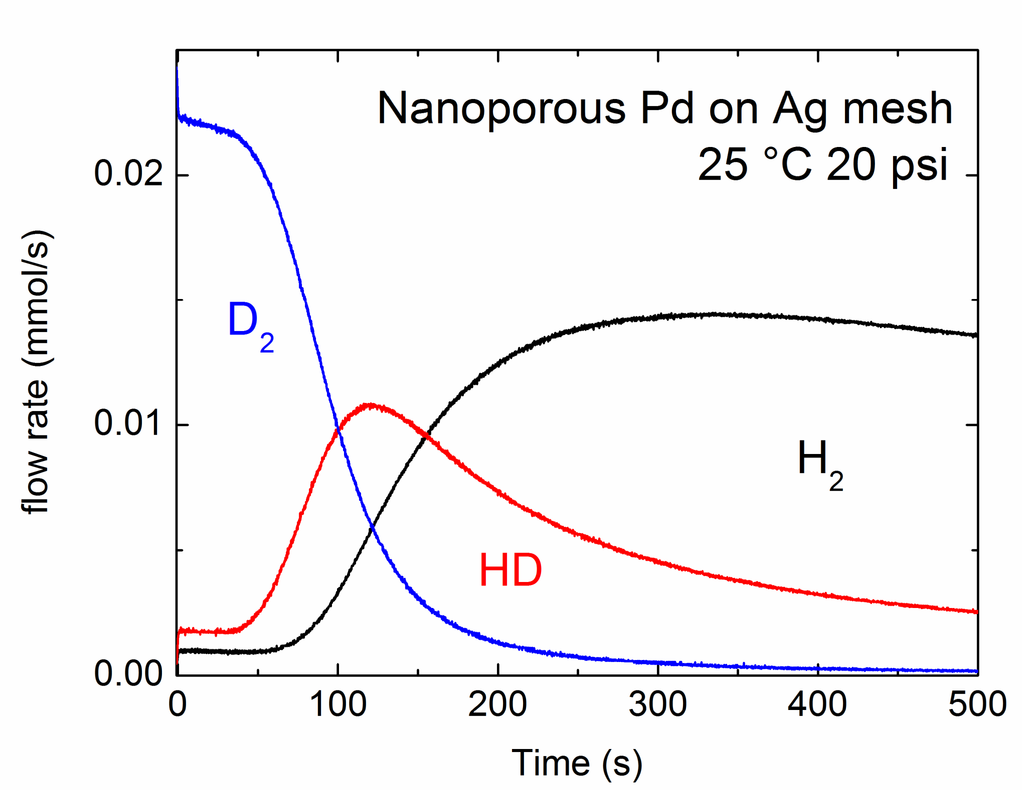




# Stacked mesh chromatography column

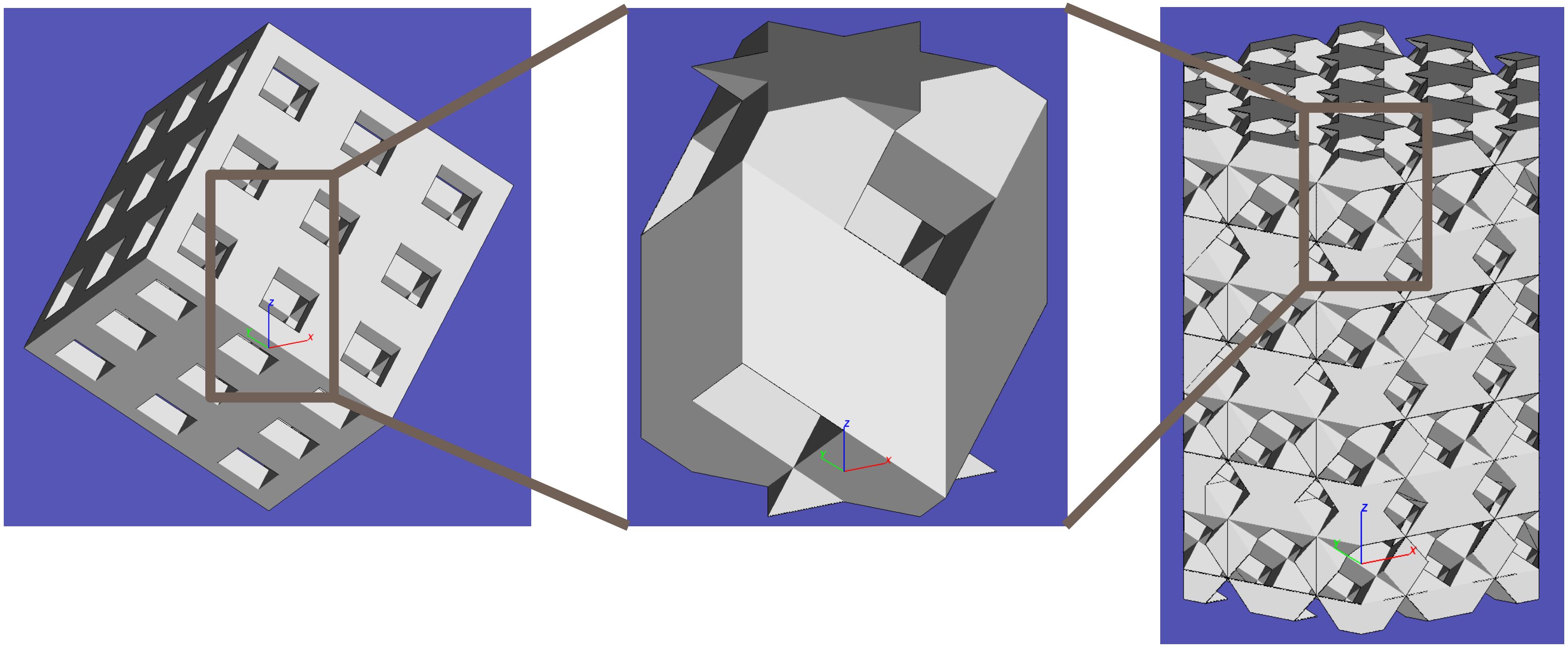
- 10 stacked mesh strips, 3x3x27mm, 598 mg Pd, 100 mg Ag
- Image by X-ray computed tomography



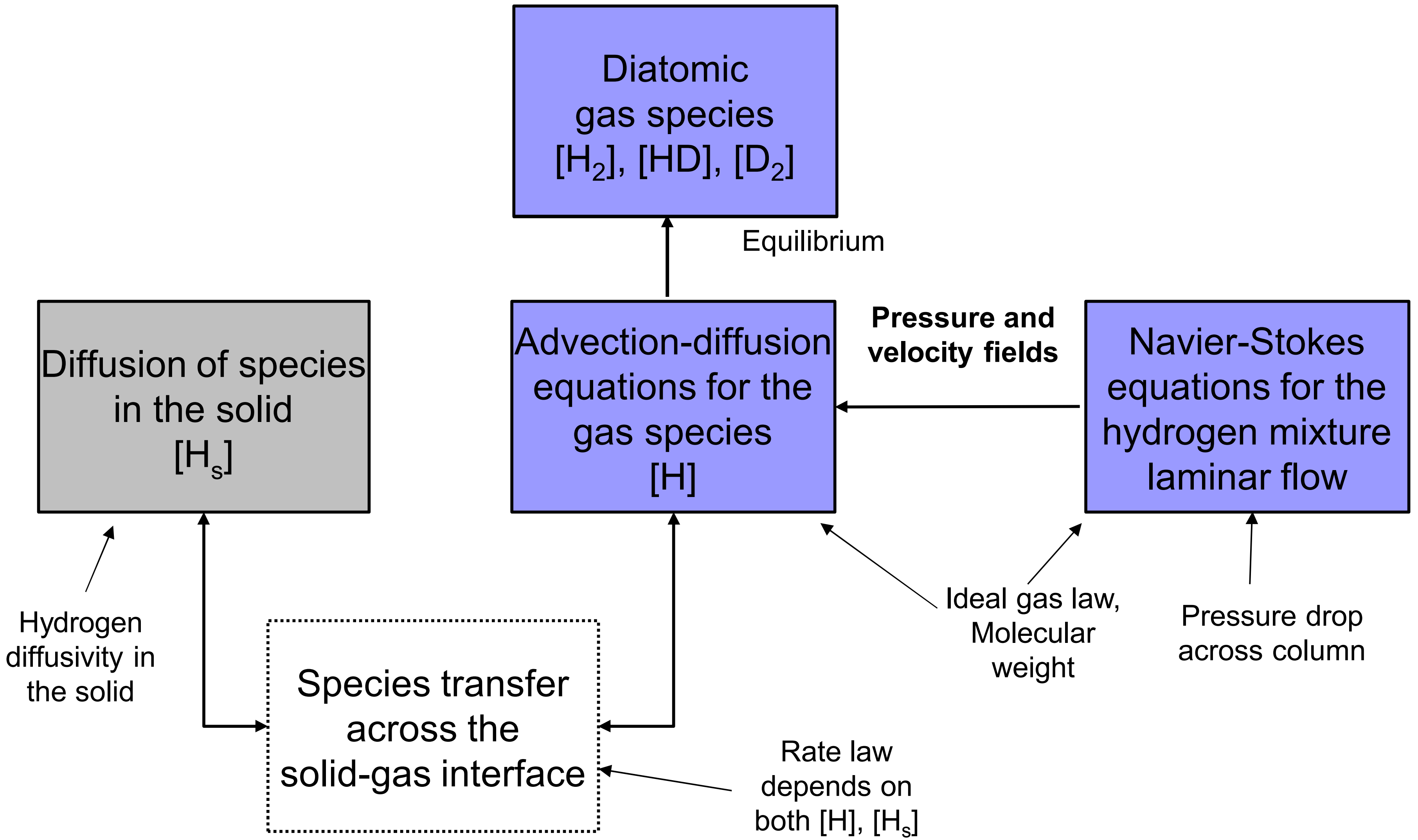



# 3D-printed porous structure

- Space diagonal-oriented cube-edge lattice
  - Simple flow paths, all at same angle vs. flow direction
  - Near their resolution limit, 3D printers are best at making simple lattices
- 5 to 50% solid fraction
- Tile hexagonal prism unit cell, crop to part shape

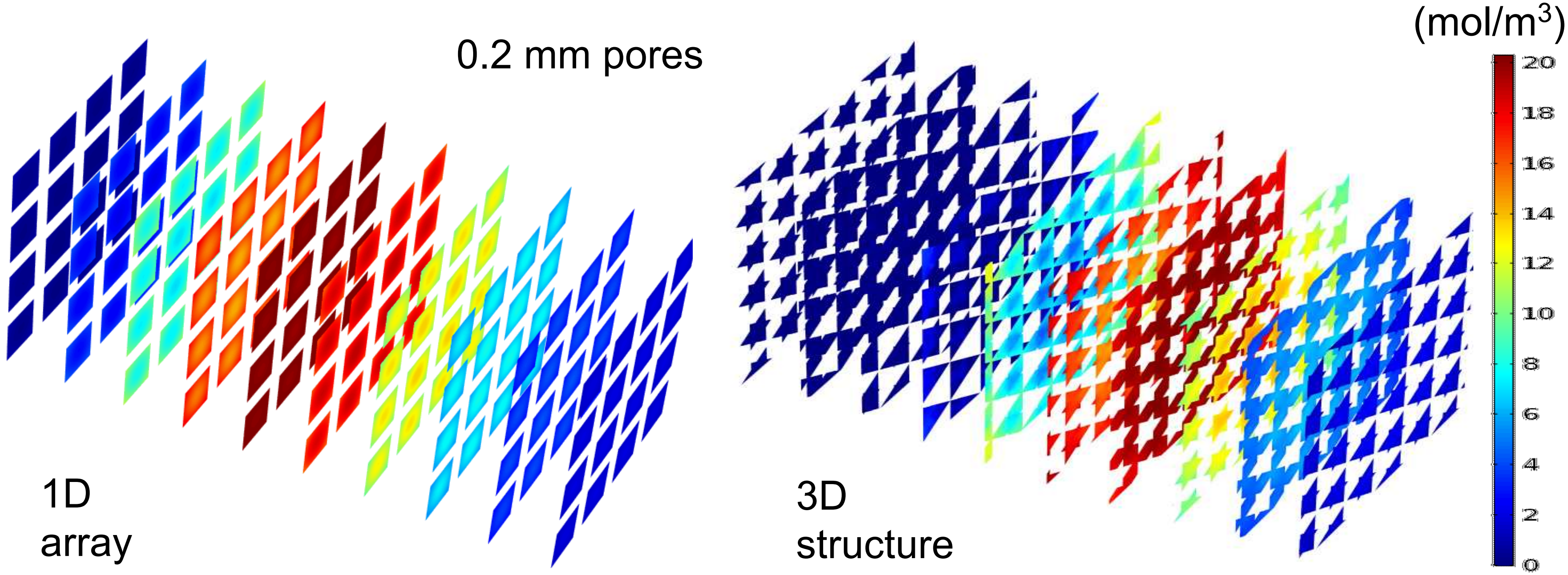


# Chromatography Model



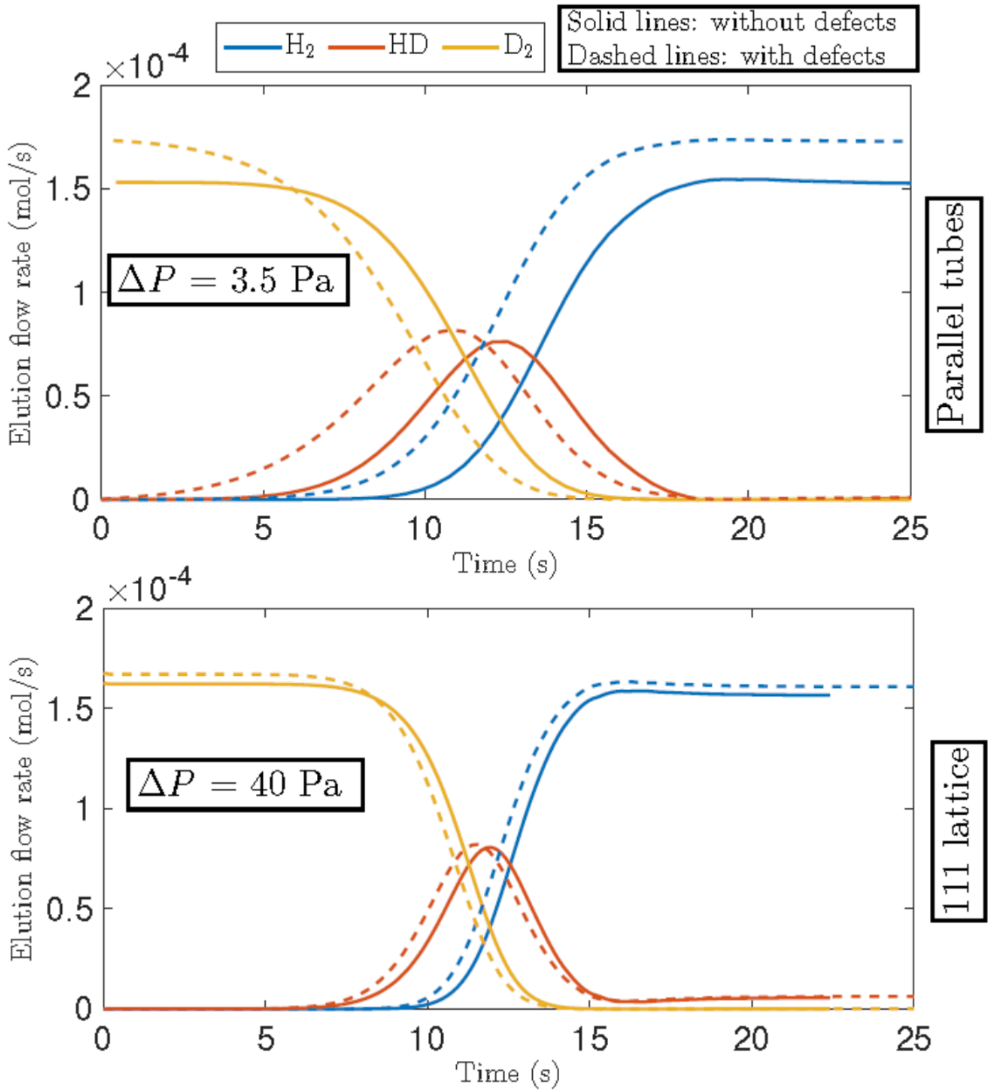
# Chromatography modeling

- COMSOL model predicts improved performance for 3D vs. 1D structures, including defect tolerance.
- This plot shows sharper HD peak for the 3D structure (right) vs. an array of straight channels (left).



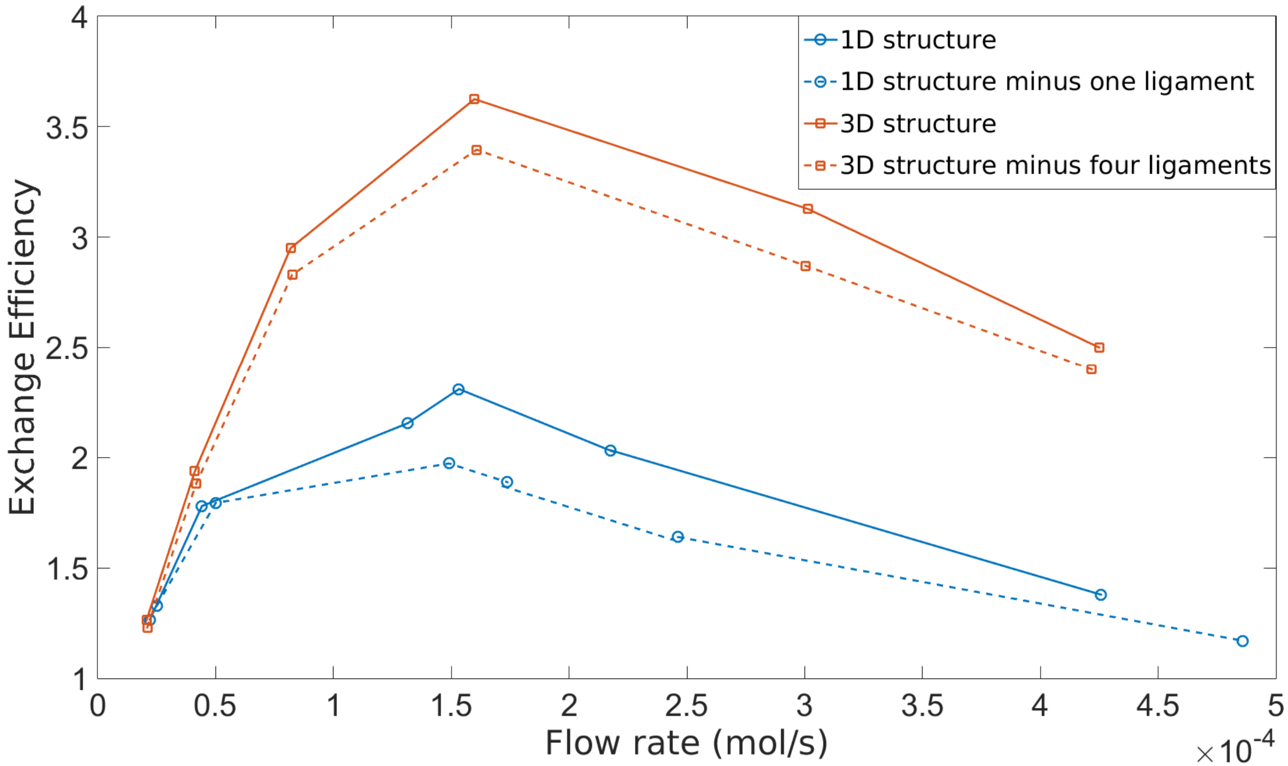
# Model 1D elution plots

- Defects lead to faster elution, broader HD peak
- 3D structure has narrower peak, lower defect sensitivity



# Model flow rate dependence

- Column length/HD peak width quantifies performance vs. flow rate, structure type.
- 3D structure outperforms 1D, even with defects present.
- Optimum flow rate exists.

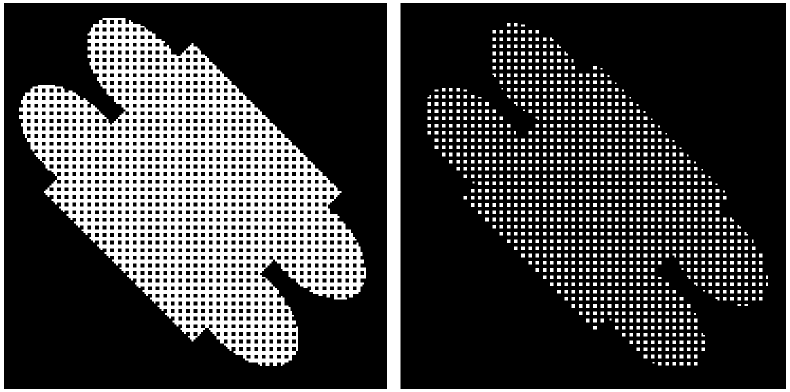


# Autodesk Ember 3D printer

- Projects blue-light images into photopolymer resin in tray through silicone-coated window
- First layer glues itself to metal base plate on z stage
- Stage moves up, tray sloshes resin, repeat 100-1000x
- Image is 912x1140 array of 50 µm pixels
- Resin contains photoinitiator, absorber, mono- and oligo-acrylate monomers
- $7k instrument, $100/L resin
- Mostly open source polymers, software, and hardware
- Window adhesion limits lattice geometries

Autodesk Ember

Image slice examples

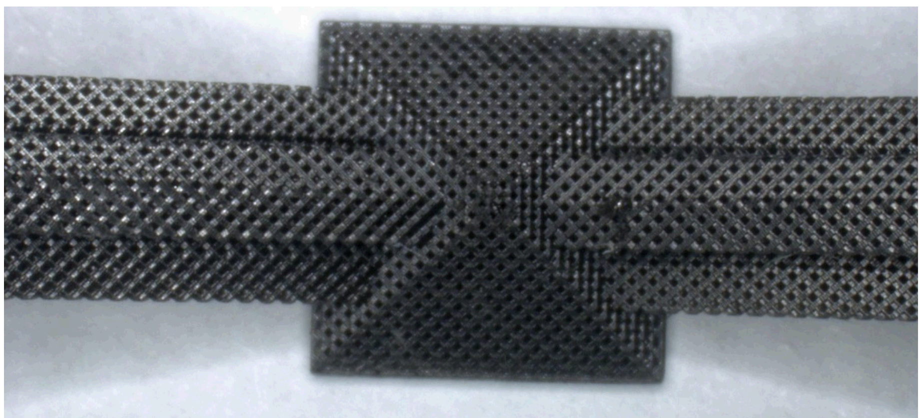


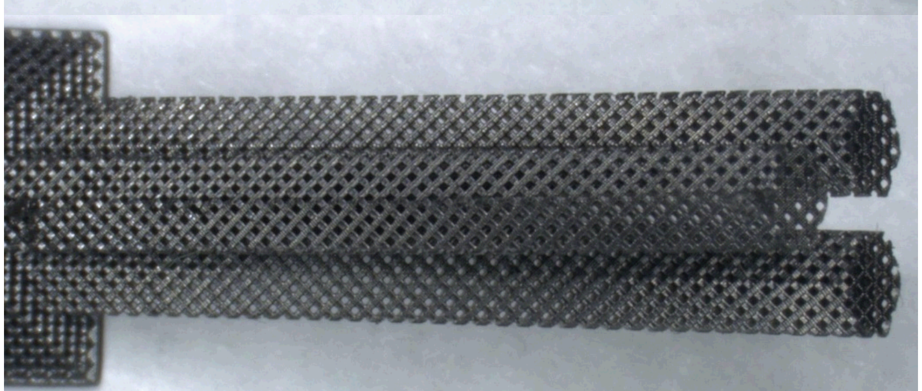
# Ember operation

- Expose, move up, slosh, repeat

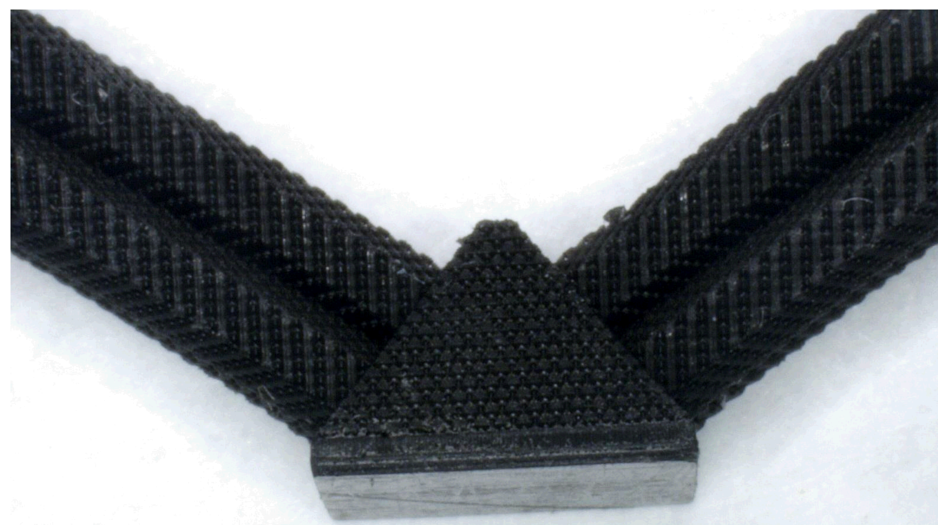
# Ember lattice

- This Ember part has 150 µm pores. The part is grown at an angle so that the cube-edge lattice is aligned with the growth direction, allowing full use of the printer’s resolution.



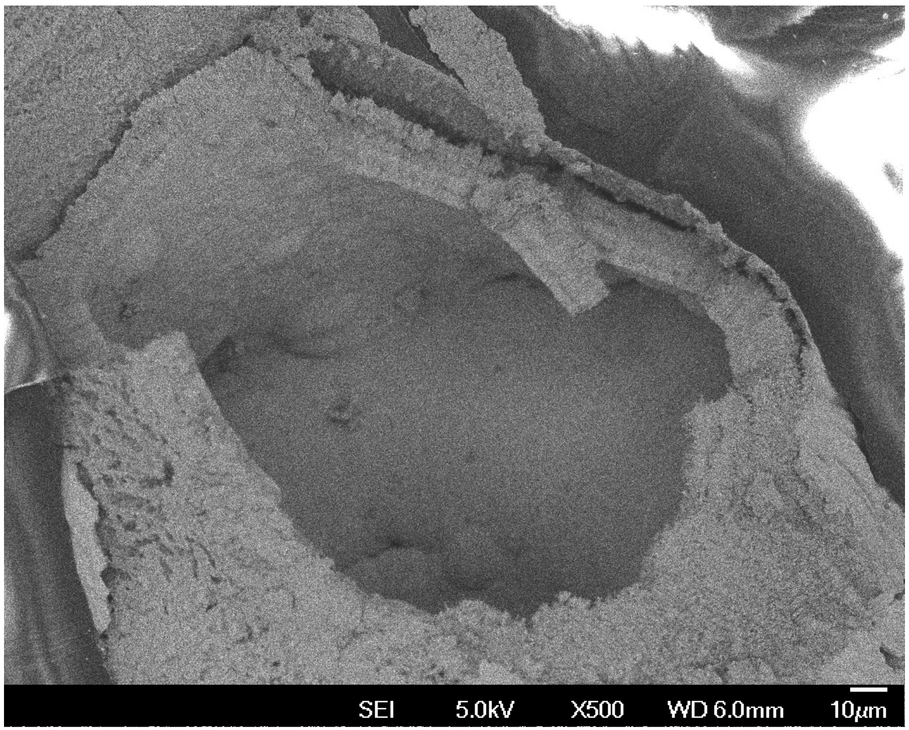


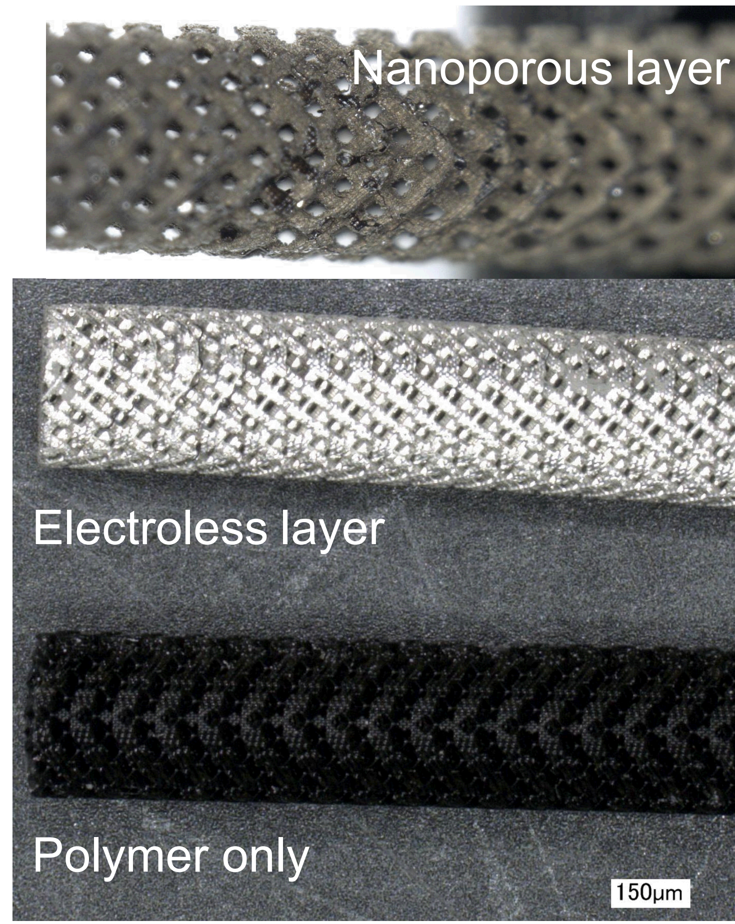
Pyramid base is 7.5 mm
Cylinders are 2 mm diameter, 20 mm long



# Metal coating of Ember part

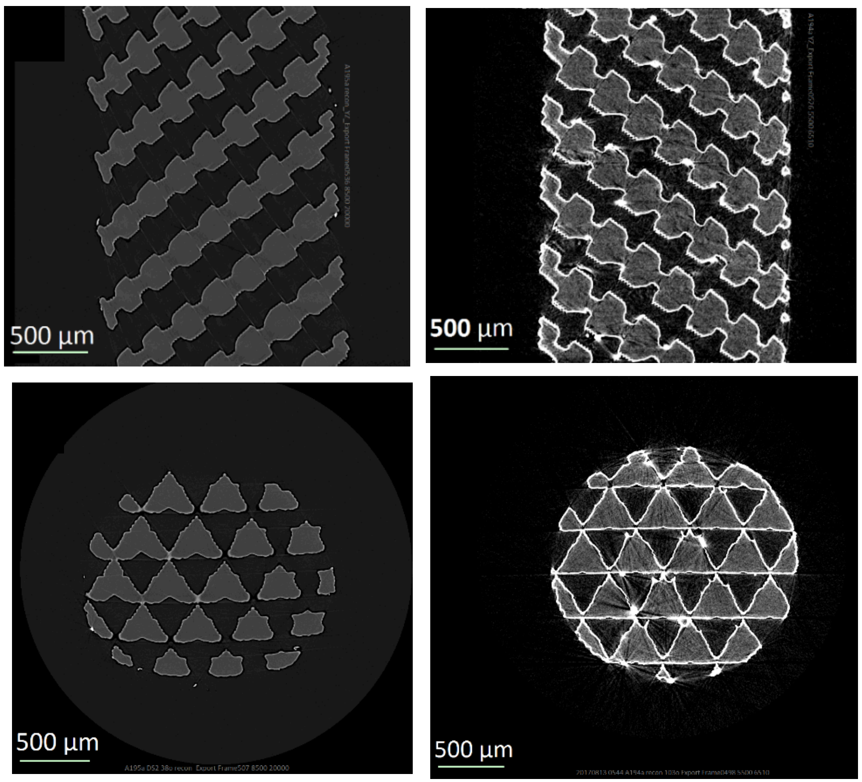
- We have grown conformal 1 µm scale Pd layers on Ember parts by electroless deposition. The layers can be thickened by subsequent electroless deposition or electrodeposition.

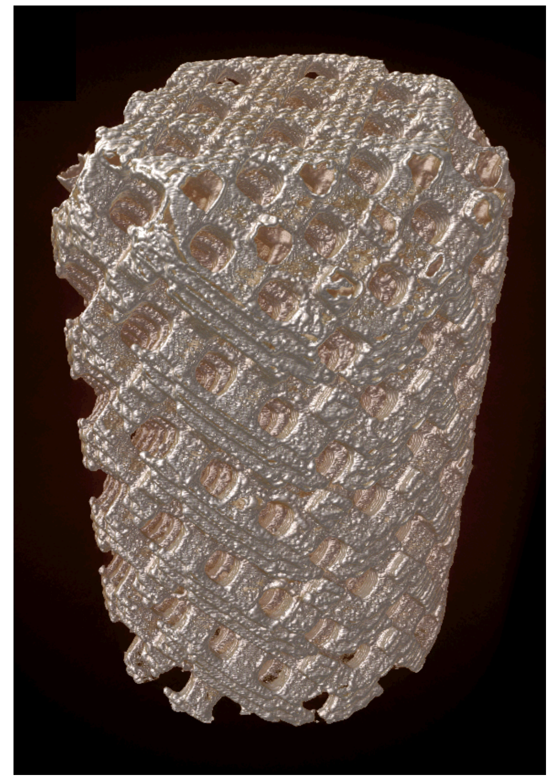


# Ember x-ray tomography

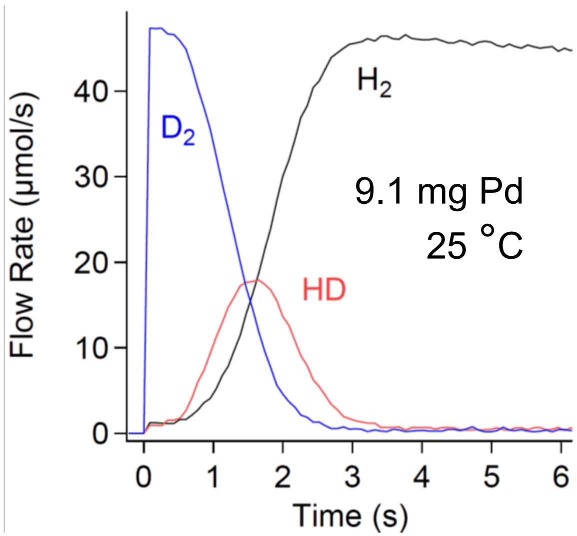
- X-ray tomography has confirmed that the electroless deposition method evenly coats the part interior.

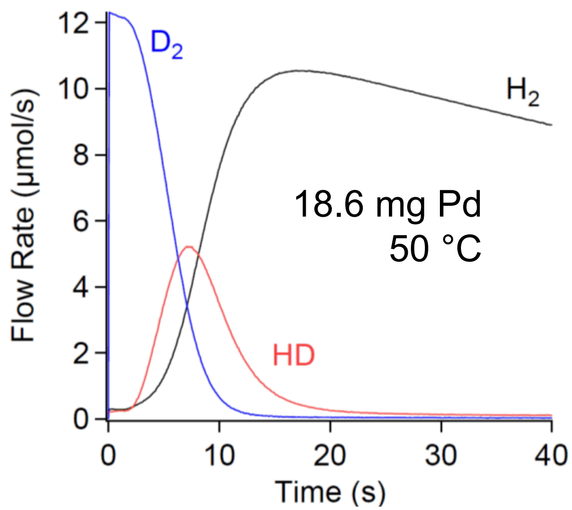


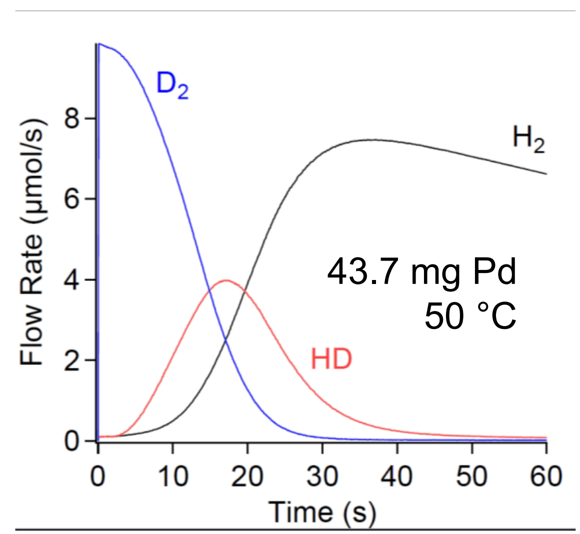



# 3D-printed column performance

- Electroless layer + porous electrodeposited layer
- Peak width approximately equals elution time
- Some nearly pure $D_2$ elutes
- Should improve with more Pd, lower polymer volume fraction
- 2 psi pressure drop

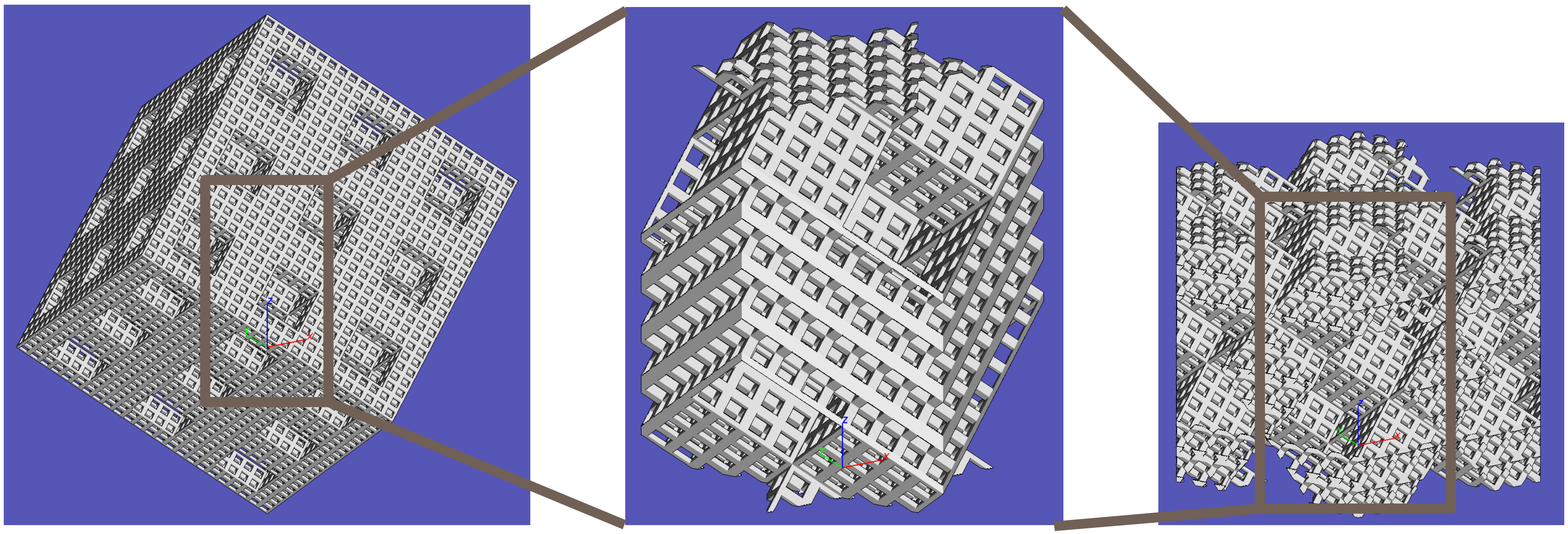



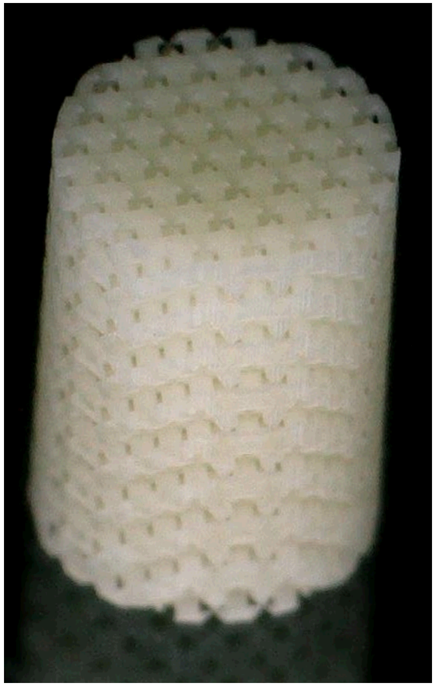
# Hierarchical lattices

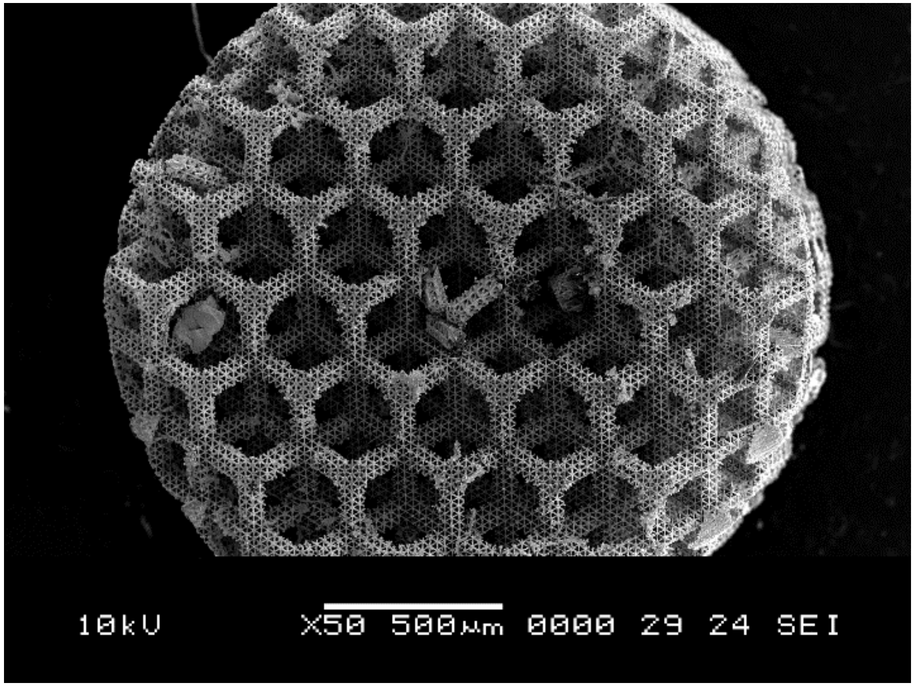
- Can finer porosity be 3D printed?
- Example: finer lattice is also a cube-edge lattice oriented along the cube space diagonal
- Finer lattice increases the surface area of the solid phase, allowing for increased fluid-solid contact.
- Metal layer can be electroless only, without nanoporous layer
- Requires high-resolution 3D printer

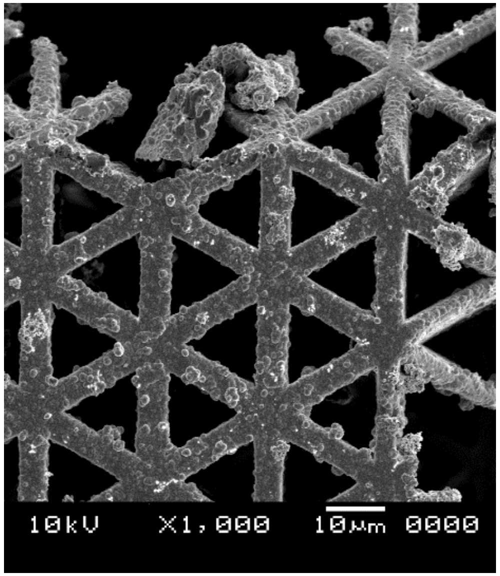


# Sparse Nanoscribe sublattice

- The Nanoscribe 3D printer uses two-photon polymerization by a rastered laser to achieve µm scale resolution, but it prints macroscopic volumes slowly.
- We have designed sparse sublattices that can print as two 2 mm diameter, 2.8 mm tall cylinders overnight (9 $mm^3$).
- Left image is a polymer structure in an optical microscope. Other images are electroless Pd-coated parts in the electron microscope.

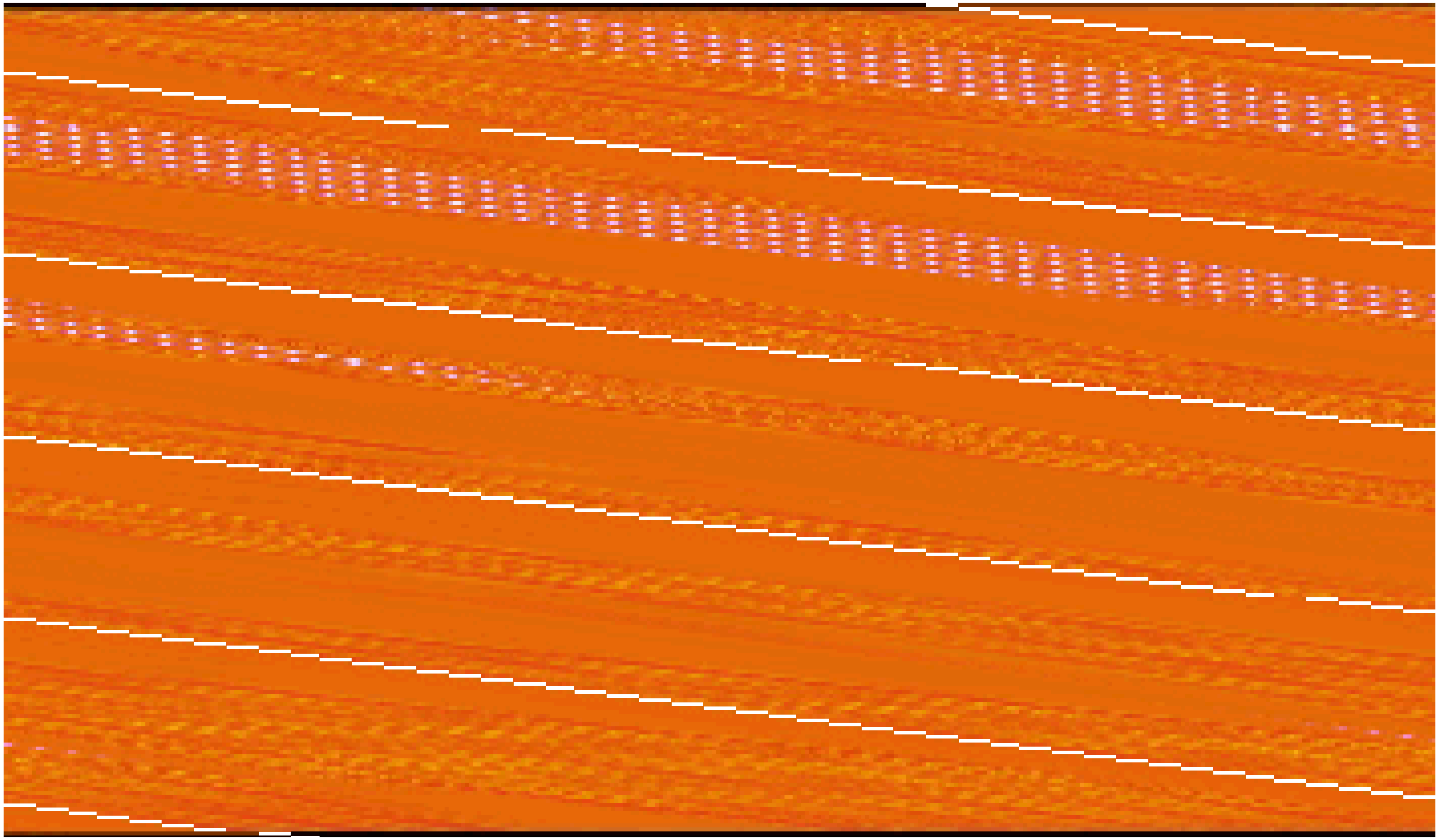




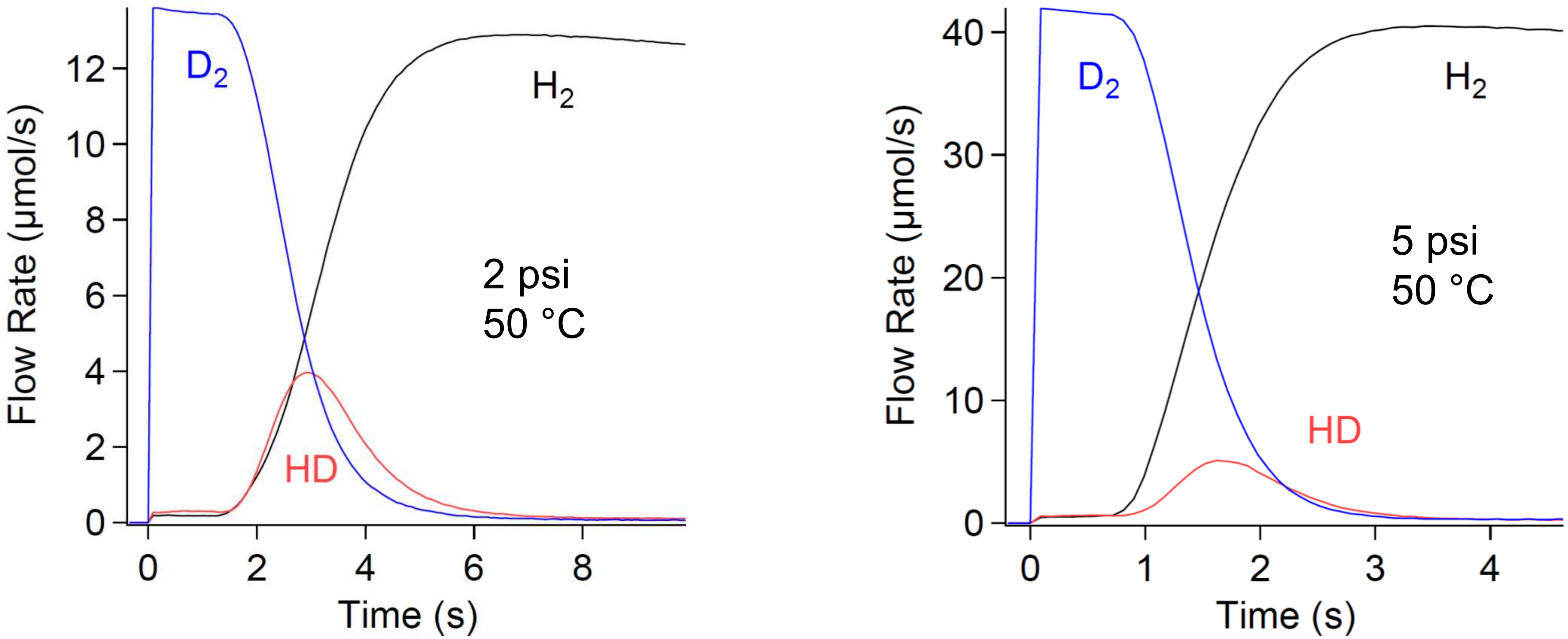
# Nanoscribe movie

- Rastered laser solidifies polymer
- µm-scale overhangs are accommodated



# Nanoscribe chromatography

- 14 mg Pd on 6 stacked parts
- HD peak may be limited by detector rise time



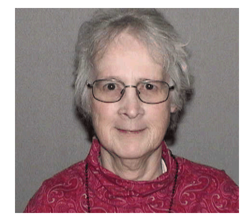
# Conclusions

- Projection stereolithography and two-photon lithography can efficiently print macroscopic parts with features on the 1-100 μm scale.
- Polymer parts can be uniformly metallized.
- Chromatography models predict sharper reaction fronts and greater defect tolerance for 3D versus 1D structures.
- Gas flow and tests show consistency with models.

# Team members

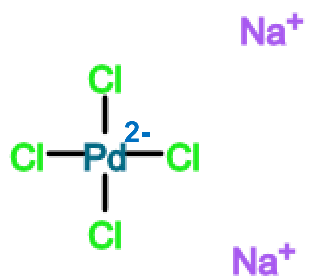
Sandia National Laboratories

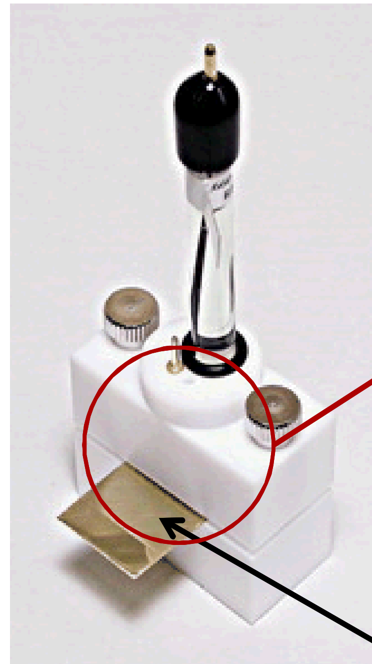
- Dave Robinson (PI)
- Maher Salloum (modeling)
- Bryan Kaehr (Nanoscribe)
- George Buffleben (flow tests)
- Ryan Nishimoto (electron microscopy)
- Bernice Mills (X-ray tomography)
- Chris Jones (metal deposition)
- Gail Garcia (electrochemistry)
- Victoria Lebegue (Ember printer)
- Aidan Higginbotham (Ember printer)
- Roopjote Atwal (Ember printer)

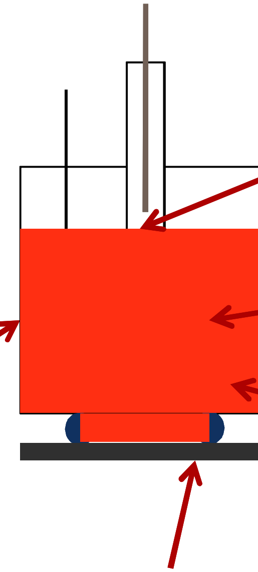




# Electrodeposition of Nanoporous Palladium

$$PdCl_4^{2-} + 2e^- \rightleftarrows Pd + Cl_4^-$$






300nm Pd on Si wafer
10nm Ti adhesion layer
Surface area: 0.4cm$^2$

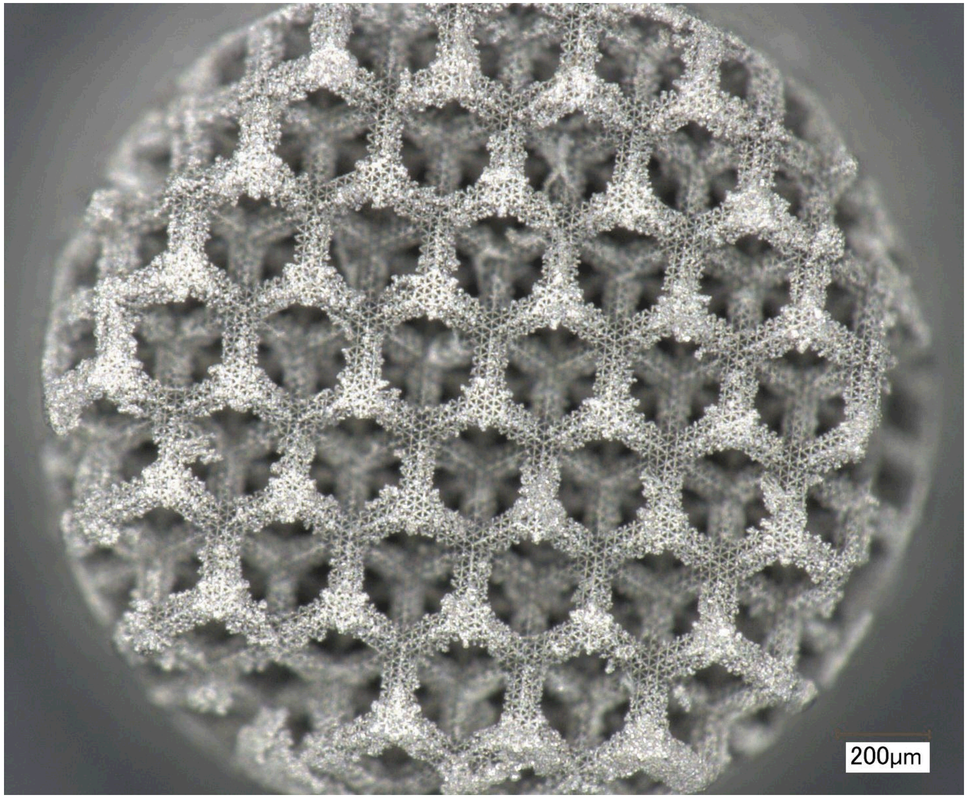
Pluronic F127 micelle former
$EO_{101}\ PO_{56}\ EO_{101}$
where $EO_2PO_2EO_2$ is :

electrolyte solution:
200µl 0.25M $Na_2PdCl_4$
200µl 1M HCl
200µl 10% F127

Apply -0.4 to -1 mA for 1-24 hours

# Nanoscribe optical images

With electroless layer




With nanoporous layer