# Using Impurities to Tailer Mesporous Metals: A KMC Study of Dealloying

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This work is supported by the

**U.S. Department of Energy, BES/HFI** under grant DE-FG02-05ER15727

**Special thanks to:**

Anant Mathur**,** Josh Snyder, Roswitha Zeis (JHU)
Yi Ding (Shandong Univ./JHU),
Mingwei Chen (Tohoku University)
K. Sieradzki (ASU), Dionisios Margetis (UMd)

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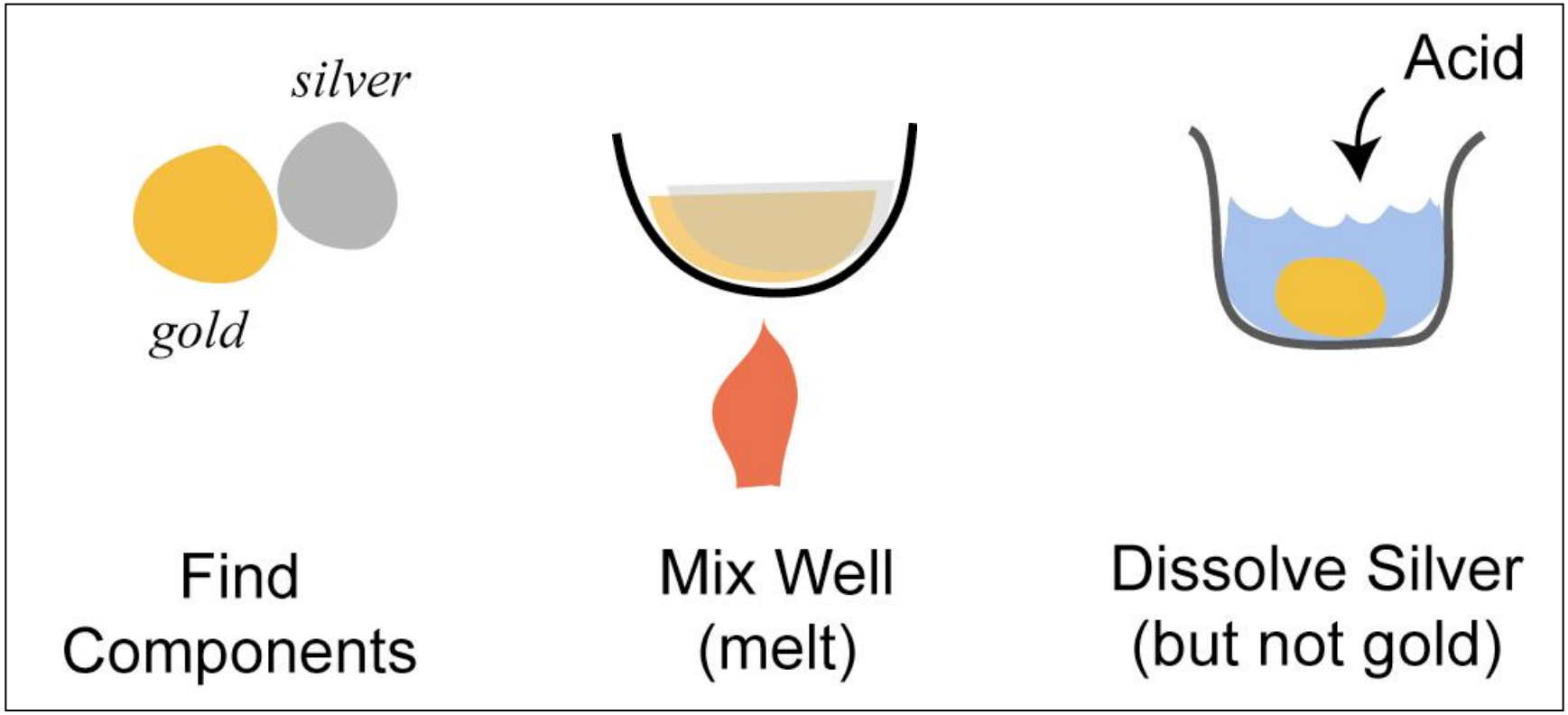
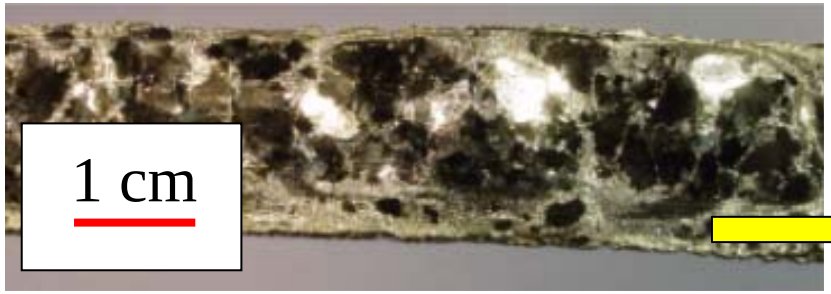
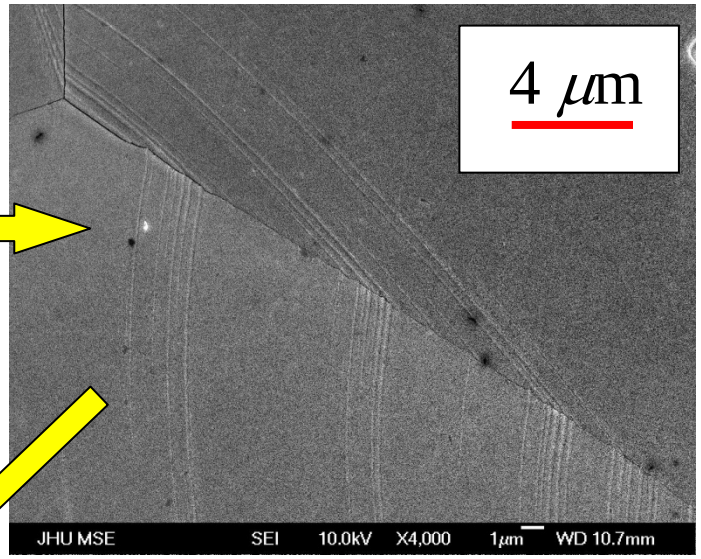
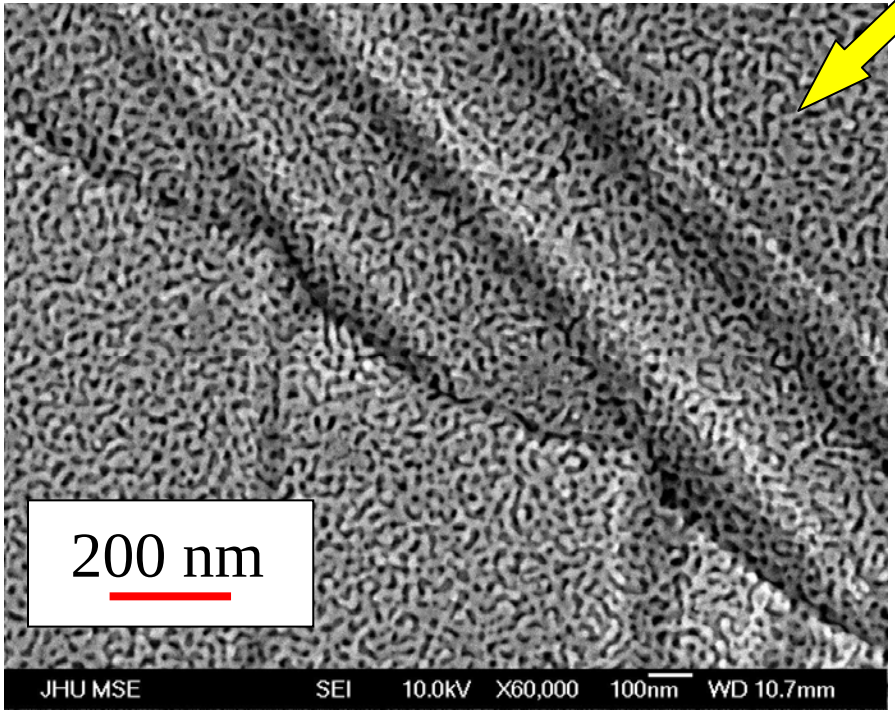
# “Nanoporous” Gold (NPG) Made by Dealloying

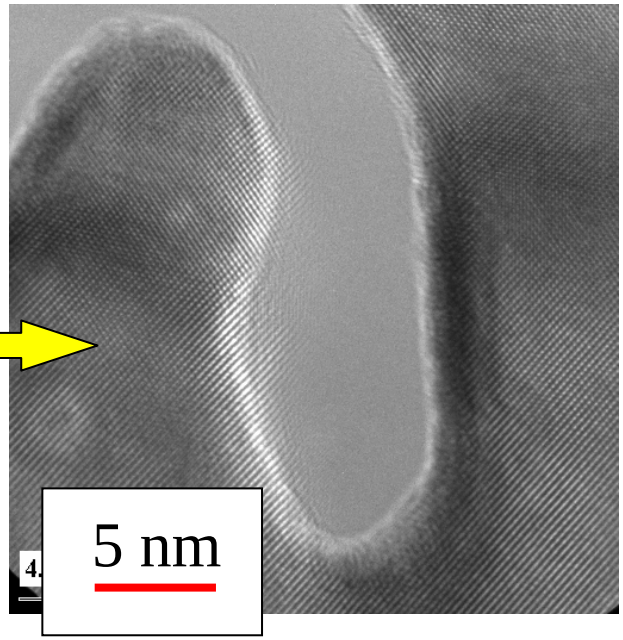


# An Example Experiment



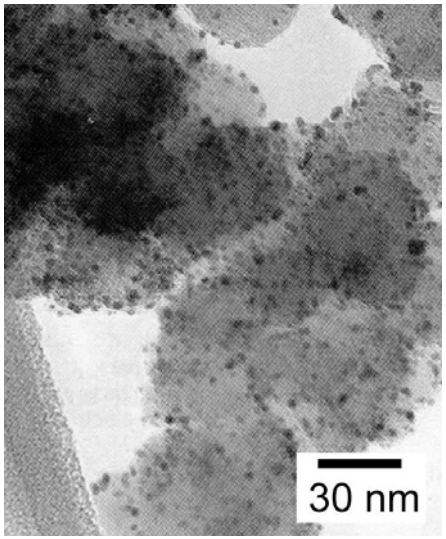
# Materials Design of Precious Metal Fuel Cell Catalysts

**Nanoparticles**

- High surface area/volume
- Immobilization by physisorption

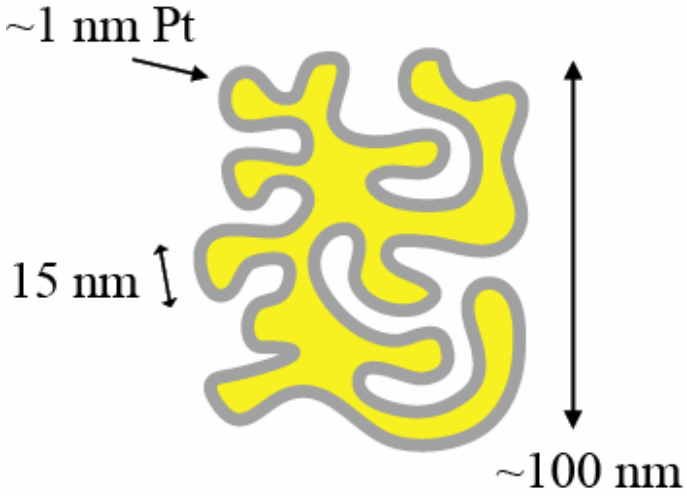
  *thermal stability issues*
- No intrinsic in-plane conductivity
- Processing leads to “thick” (>10 microns) catalyst layers

  *precious metal utilization/waste*



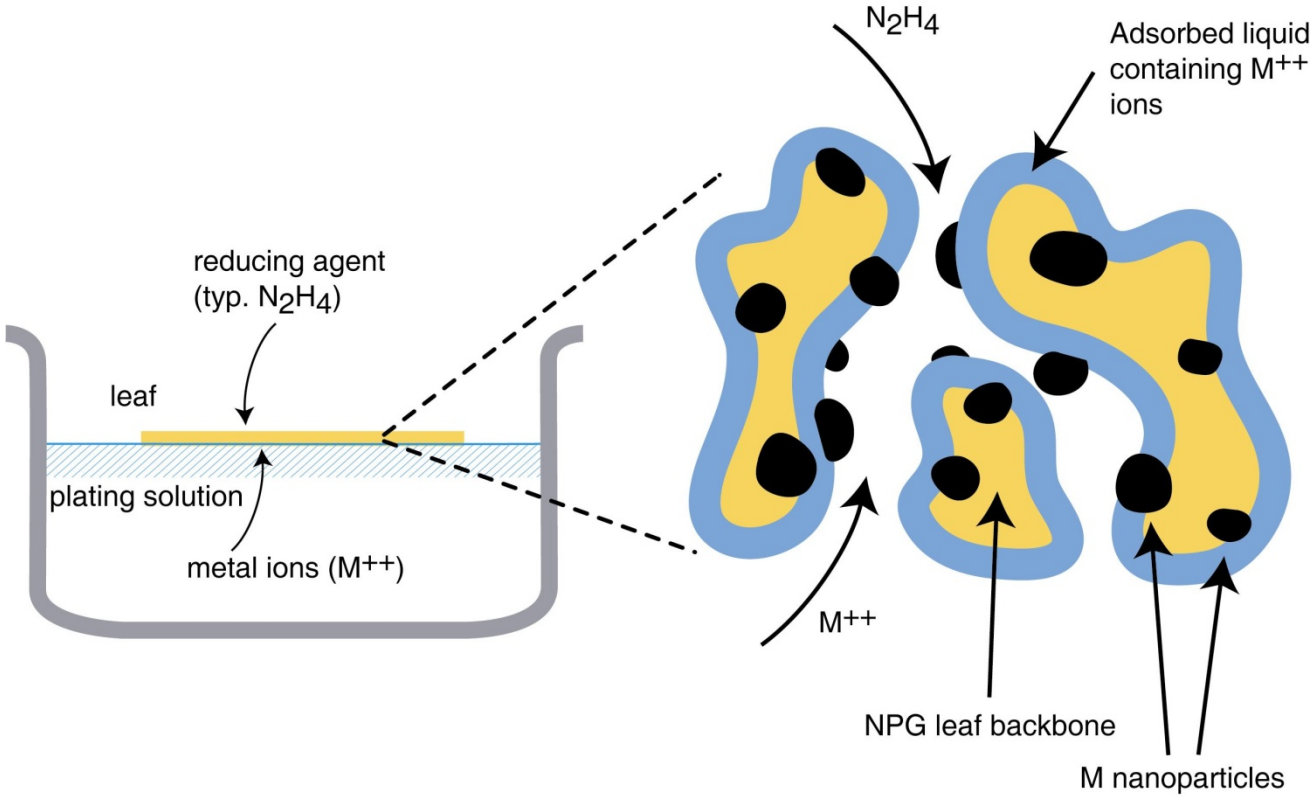

**Mesoporous Metal Membranes**

- High surface area/volume
- Immobilization by epitaxy
- High intrinsic in-plane electron conductivity
- Processing could (does!) lead to thin (100 nm) catalyst layers



# Electroless Plating of NPG Leaf to Form Electrocatalytic Nanocomposites

Use a thin porous gold membrane ("leaf") floating on water.

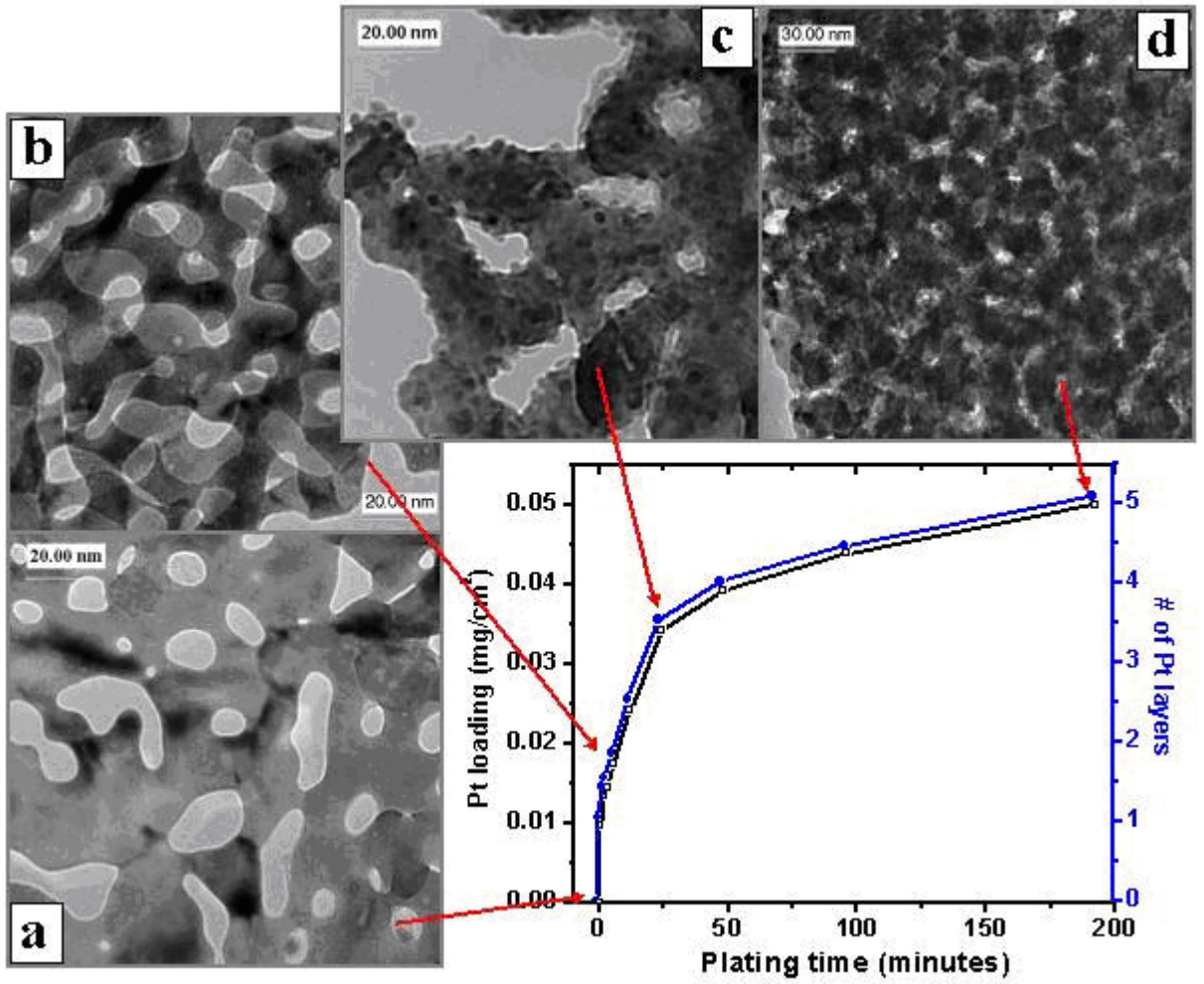



Plating is confined to within the pores, and self-limits

-- an advantage over typical electroless or electrochemical plating

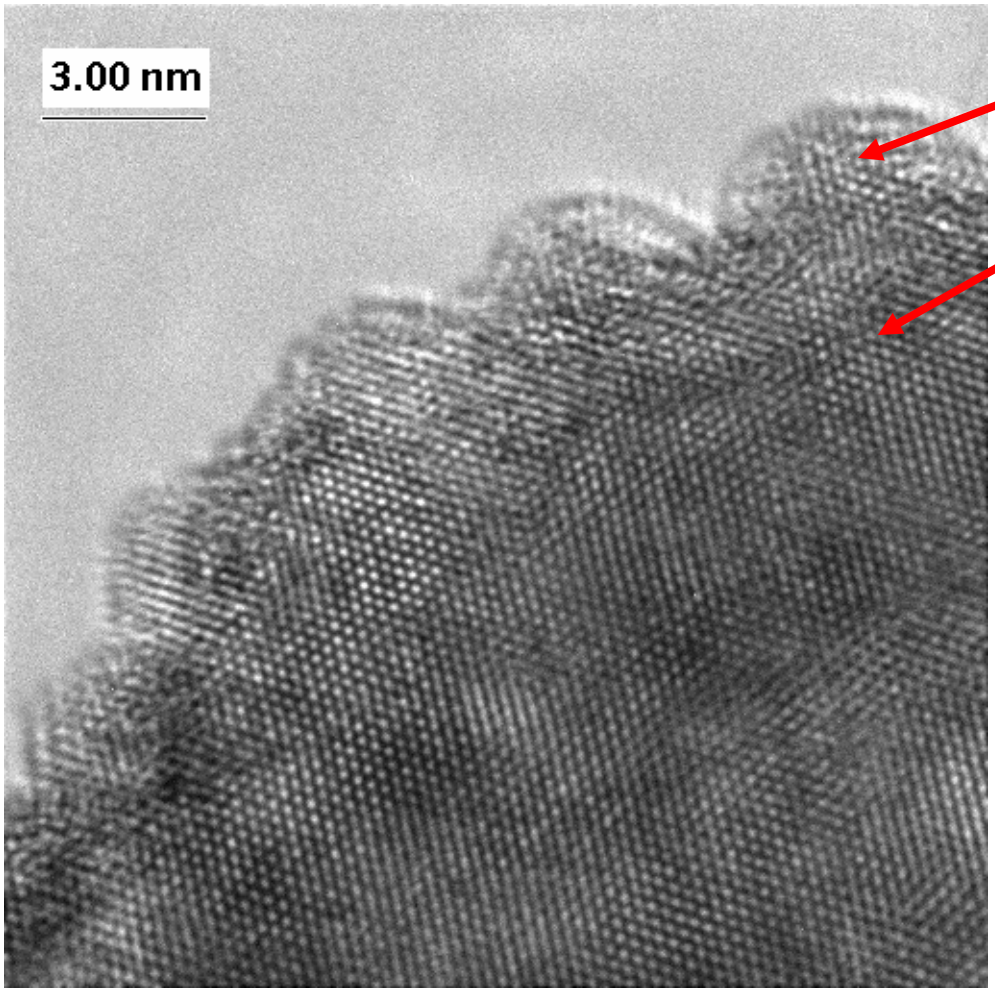
To date, we have plated **Pt**, Ni, Co, and **Ag**

# Growth Kinetics of Pt-NPGL




*Deposition may be controlled to within 0.01 mg/cm$^2$ (1 ml) using only room temperature benchtop chemistry. Deposition stops prior to filling of pores. (?!)*

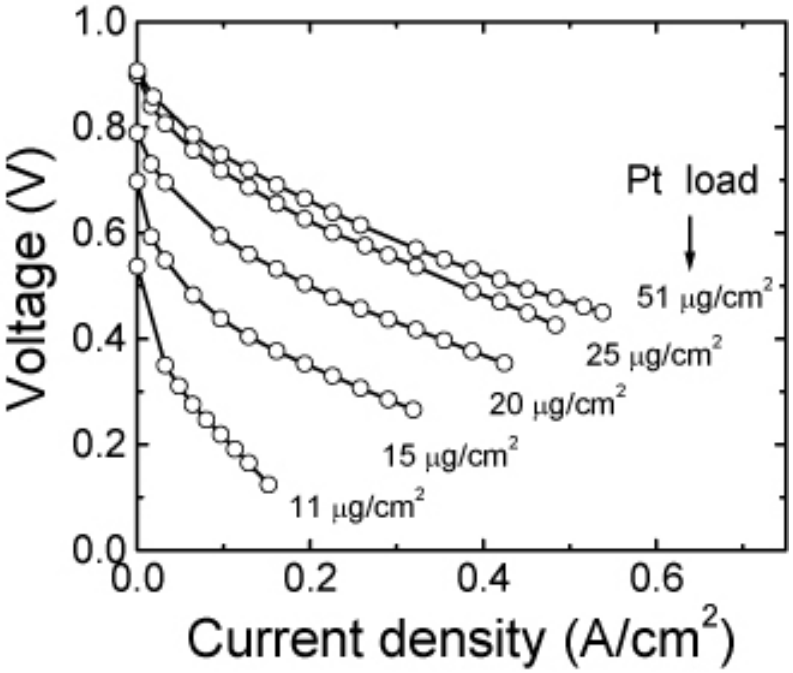
# HRTEM of Pt-NPGL

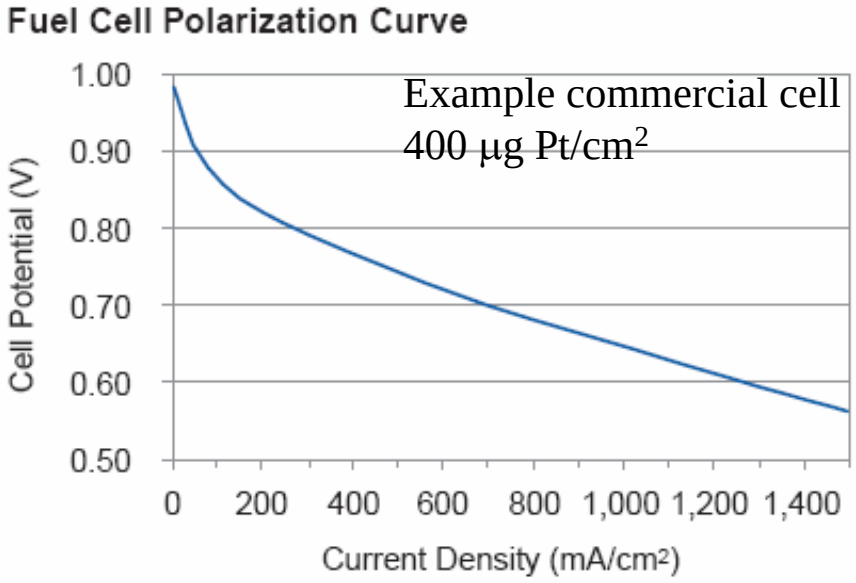



Characteristics of Islands:

- *uniform island diameter (~5 nm)*
- *narrow size distribution*
- *good epitaxy with few misfit dislocations*

# Fuel Cell Performance of Pt-NPGL

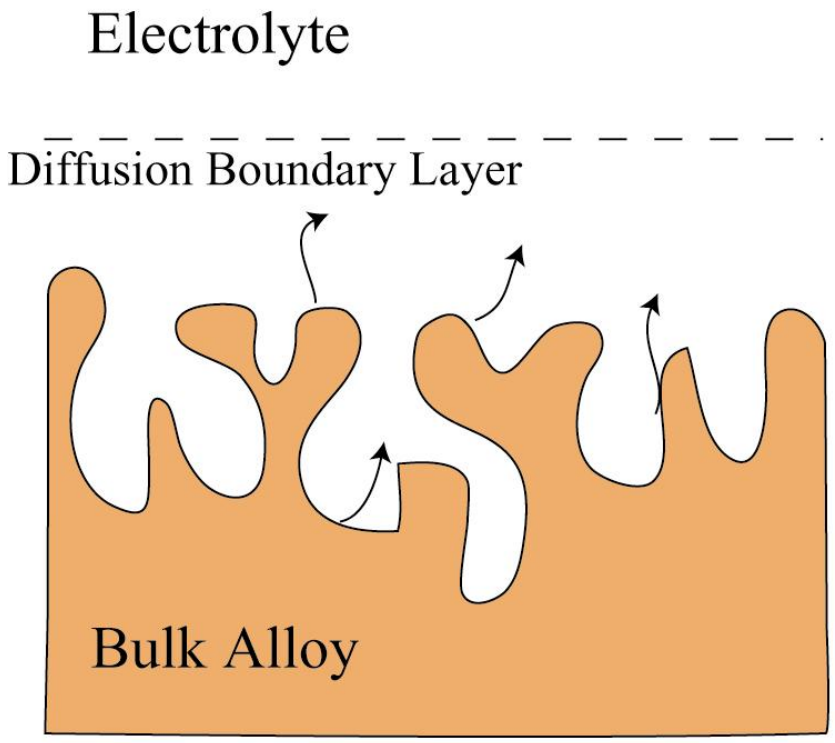



Pt-NPGL does well – ***but can we do better?***

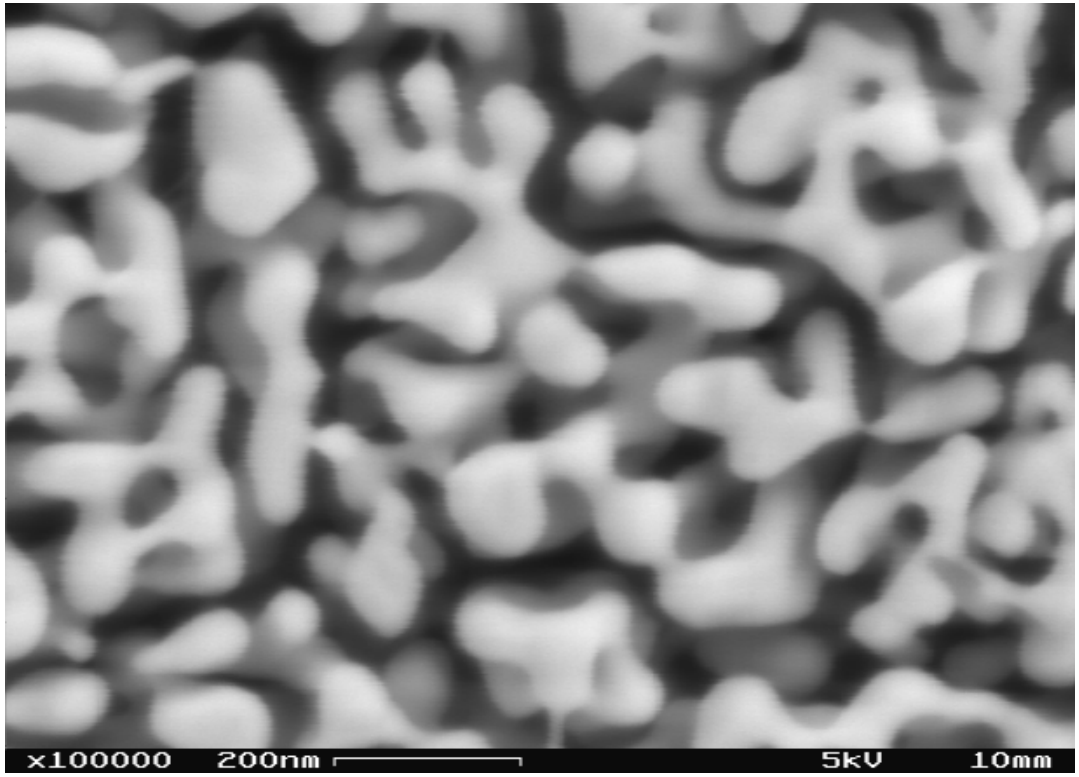
- Can we prevent coarsening?
- Can we increase the surface area/volume?
- Can we ease processing?

# Multiscale Complexity of NPG Formation




- Diffusion Boundary Layers ($\mu$m - cm)
- Mechanical Properties of Solid (> mm)
- Surface Diffusion Kinetics (< nm)
- Transport Through Nanochannels (nm - mm)
- Chemical Dissolution Kinetics (< nm)

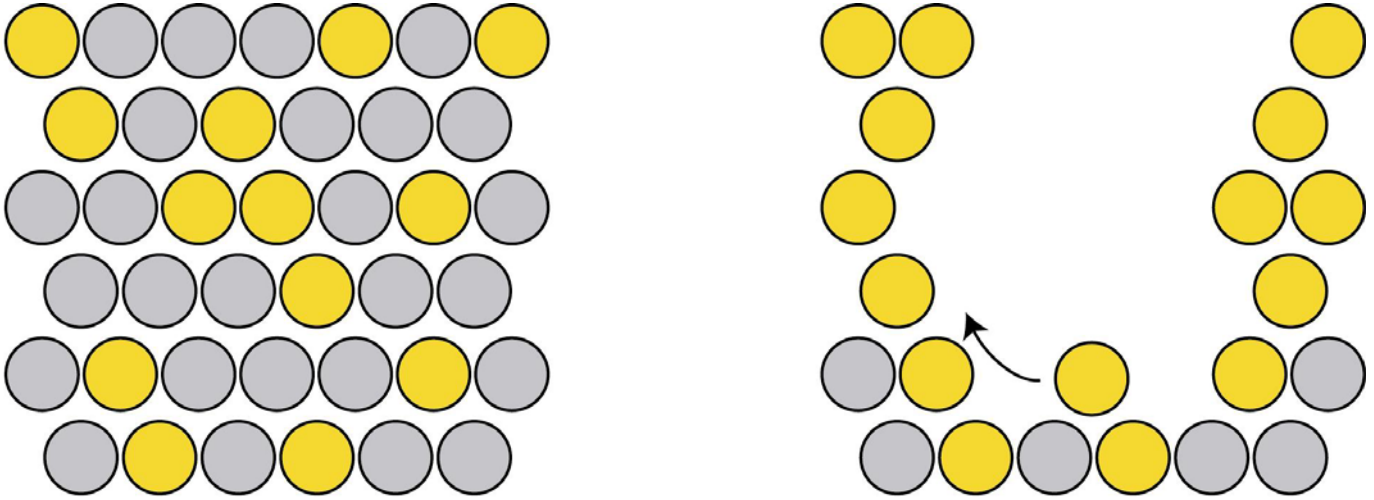
# A Useful Observation




Porosity formation implies the rate-limiting behavior is on the solid, alloy side

*diffusion limited dissolution (in electrolyte) would lead to electropolishing*

# Fast Interfacial Diffusion



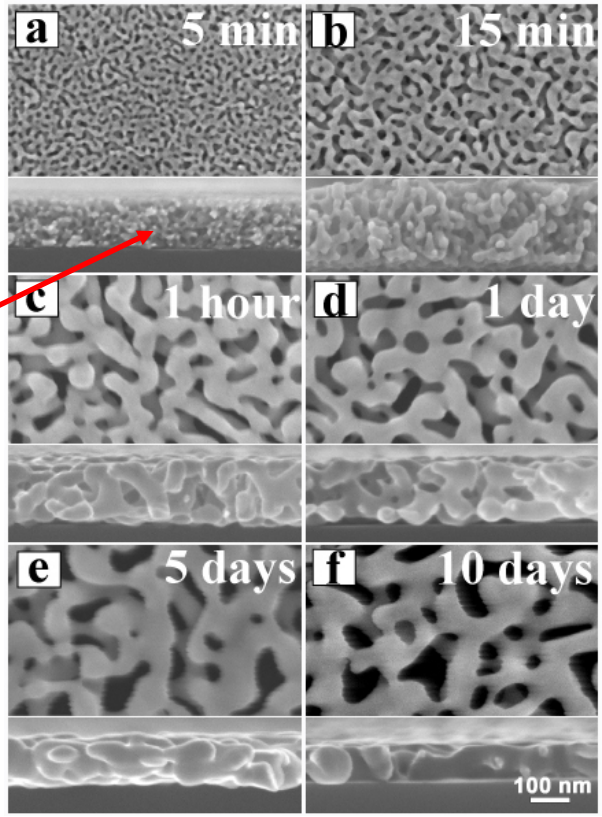
Original Alloy: 33% Gold

Observation: During dealloying, gold atoms move from their original lattice sites

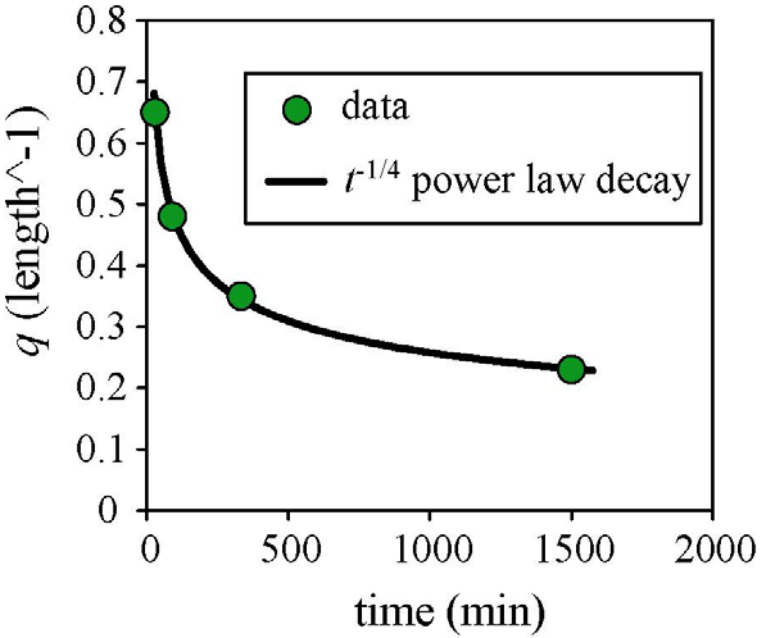
Gold atoms must diffuse along the alloy/electrolyte interface, and fast!

# Gold Surface Diffusion : “Electrochemical Annealing”

Surface self-diffusion of fcc metals in electrolyte is 5-6 orders of magnitude faster in electrolyte than in vacuum.




***note flat surfaces, uniform porosity***

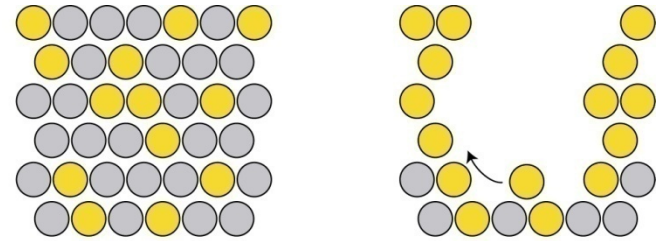



*leaf held in nitric acid for different times*

**Conclusion**: surface diffusion is fast enough to get gold atoms out of pits over experimental timescales. Why? I don’t know.

Y. Ding, Y.-J. Kim, J. Erlebacher, “"Nanoporous Gold Leaf:"Ancient Technology"/Advanced Material”, *Adv. Mat.*, **16** (2004), 1897.

# NPG: The Fundamental Problem



Original Alloy: 33% Gold

## EXPECTATION

Gold atoms SHOULD diffuse in a direction so as to

(a) smoothen the surface (capillary action)

*or*

(b) oppose concentration gradients

Flat surfaces passivated with pure gold

## OBSERVATION

Gold atoms DO diffuse in a direction so as to

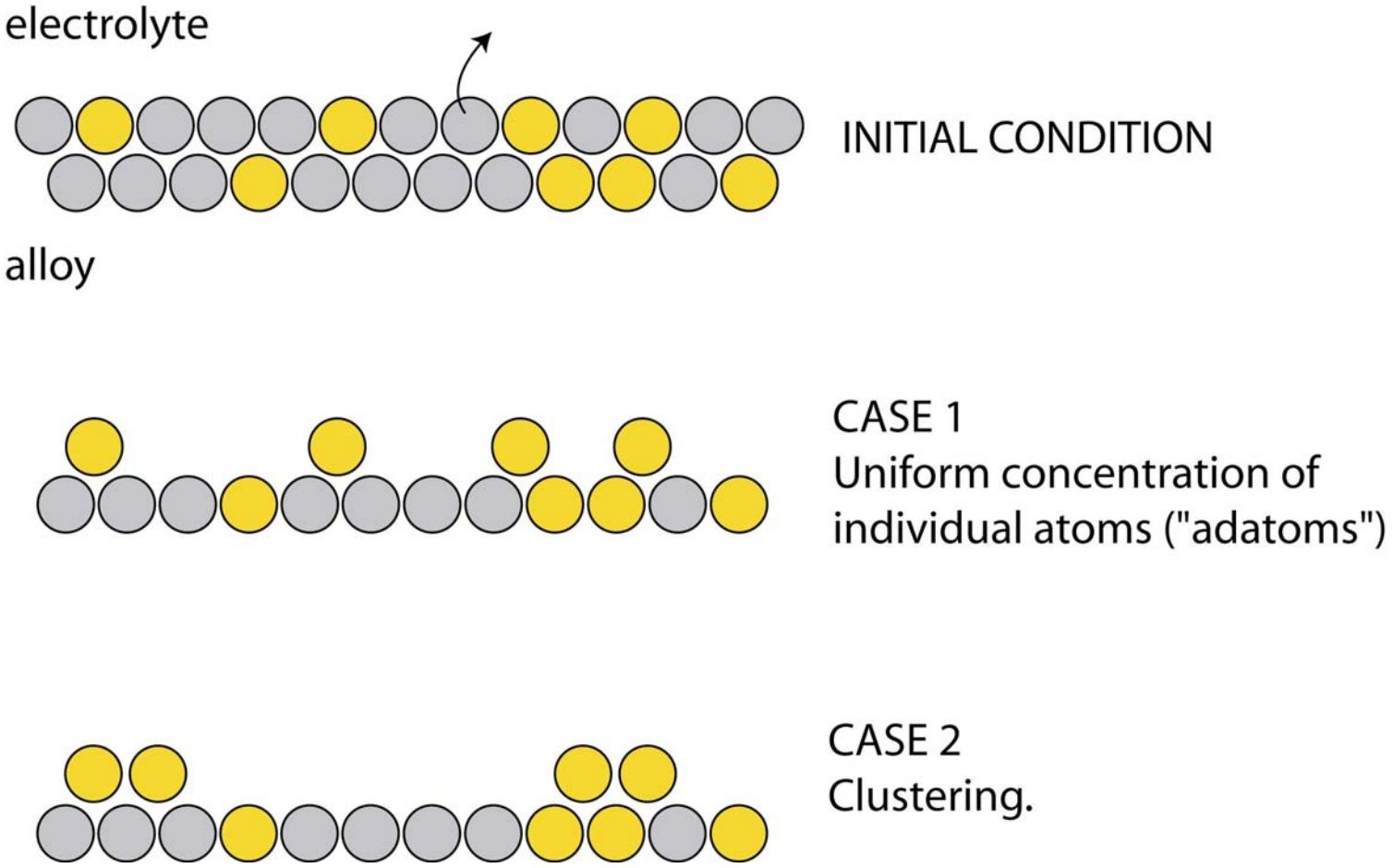
(a) Allow pores to grow and increase the total surface area

*and*

(b) Keep the pits from becoming clogged with gold

Highest surface area connected metals known to mankind

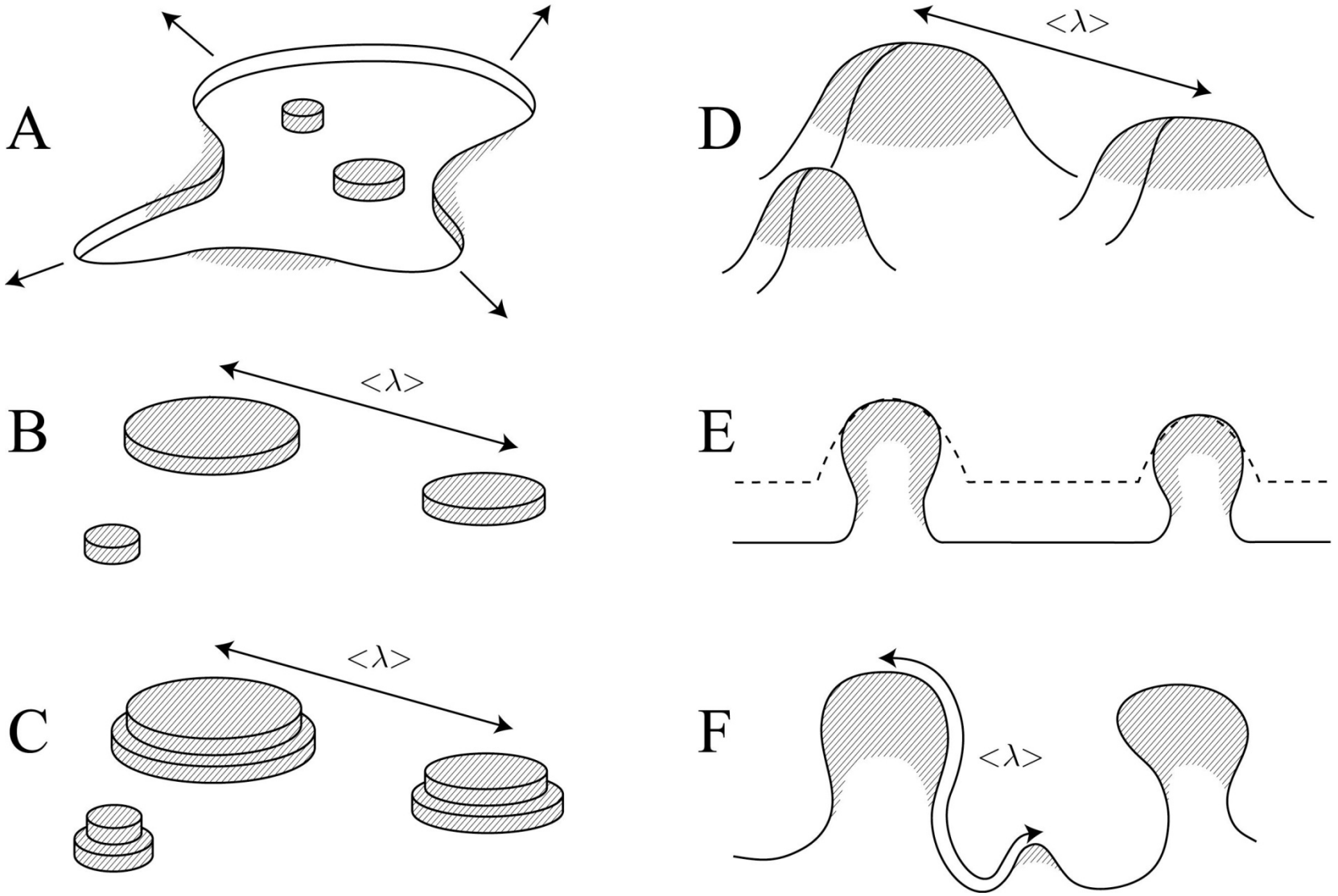
# NPG: Solution to the Fundamental Problem




Agglomeration of gold atoms to channel walls is due to thermodynamics favoring clustering of adatoms on the alloy/electrolyte interface → describable using the formalism of 2-d spinodal decomposition on the interface

J. Erlebacher, M.J. Aziz, A. Karma, N. Dimitrov, K. Sieradzki, "Evolution of nanoporosity in dealloying," Nature **410** (2001), 450.

# Qualitative Model of Porosity Evolution in Dealloying




Erlebacher, J., "An Atomistic Description of Dealloying: Porosity Evolution, the Critical Potential, and Rate-Limiting Behavior," J. Electrochem. Soc. **151** (2004), C614

# Thermodynamics of the Alloy/Electrolyte Interface I

Or, why gold atoms get out of the way of pits.

- We model the interface as a two-species mixture on the surface of the alloy
  - "Au adatoms" and "electrolyte"
- Examine the free energy of the mixture vs. Au coverage

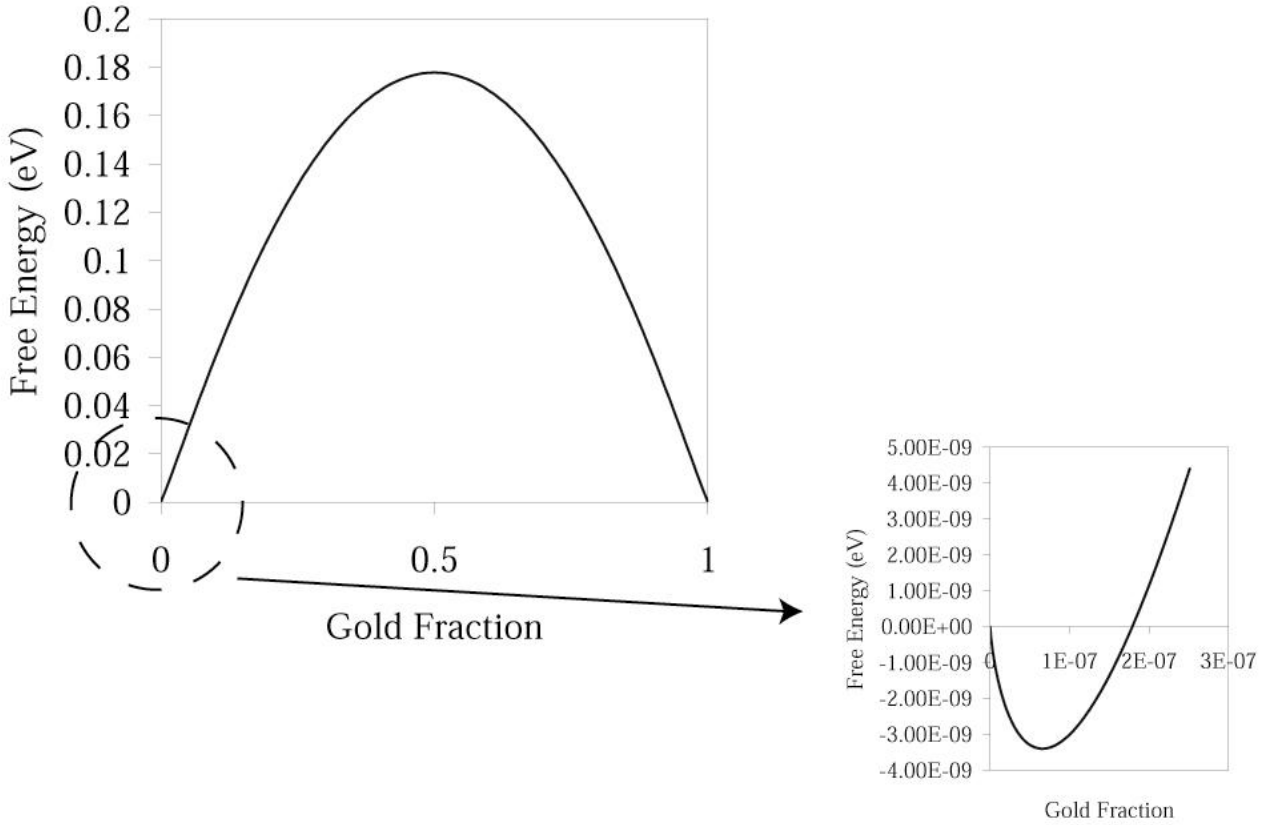
$$f(C_{Au}) = u - Ts$$

Au-Au bond energy
Au-"electrolyte" bond energy
"electrolyte"-"electrolyte" bond energy

ideal entropy of mixing

$$f(C_{Au}) = wC_{Au}(1 - C_{Au}) + k_B T\left[C_{Au}\ln C_{Au} + (1 - C_{Au})\ln(1 - C_{Au})\right]$$

# Thermodynamics of the Alloy/Electrolyte Interface II



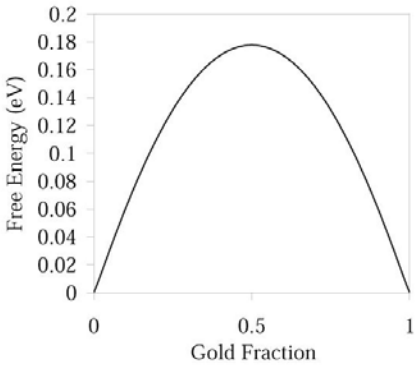

Gold *really* doesn't want to be left as adatoms

→ this drives agglomeration and diffusion out of pits

→ coarsening and capillary action occur on longer time scales

# Kinetics of Diffusion in the Au-Electrolyte Interfacial Region

- Generalized diffusion equation $\frac{\partial c}{\partial t} = M \frac{\partial^2 f}{\partial c^2} \nabla^2 c$
- Compare to usual (Fick's Law) Diffusion Eq. $\frac{\partial c}{\partial t} = D \nabla^2 c$




$$\frac{\partial^2 f}{\partial c^2} < 0 \Rightarrow \text{"Uphill Diffusion"}$$

Behavior leads to a characteristic island spacing
– "interfacial spinodal decomposition"

$$J_S = - M(C_{Au})\left(\partial_c^2 f \partial_s C_{Au} - w \partial_s \partial_s^2 C_{Au}\right)$$

# Analytic Description of Porosity Evolution

- Mass conservation $\left.\P_t C\right|_n = v_n C_0 - v_n k C - \tilde{N} \times J_S(C)$

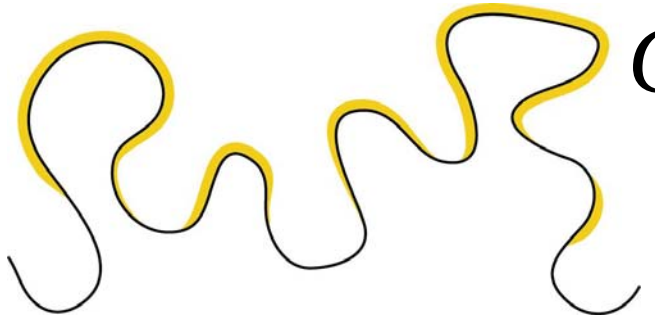
Rate at which gold from the bulk (concentration $C_0$) accumulates on the surface due to etching

Rate at which gold dilutes due to interface stretching (a geometric constraint)

Rate at which gold diffuses on the surface

$k > 0$ $\kappa$: curvature

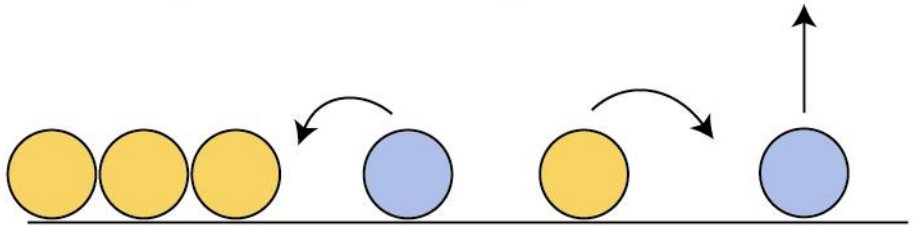
$k < 0$



# Kinetic Monte Carlo (KMC) Model for Porosity Evolution

- Concentrate on the interface
- “gold atoms” and “silver atoms”
- Allow all atoms to diffuse
- Allow only silver-colored atoms to dissolve
- Correct crystallography (fcc)
- “100-million” atom simulations

*Only silver atoms get dissolved into electrolyte*



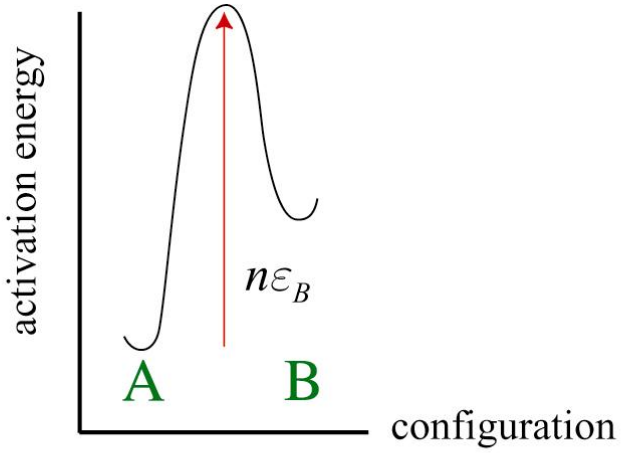
*Both silver and gold atoms diffuse*

# Kinetic Rate Laws for Diffusion and Dissolution

*Diffusion of All Species*

$$k_{A\to B} = \nu_D \exp\left[-\frac{n\varepsilon_B}{kT}\right]$$

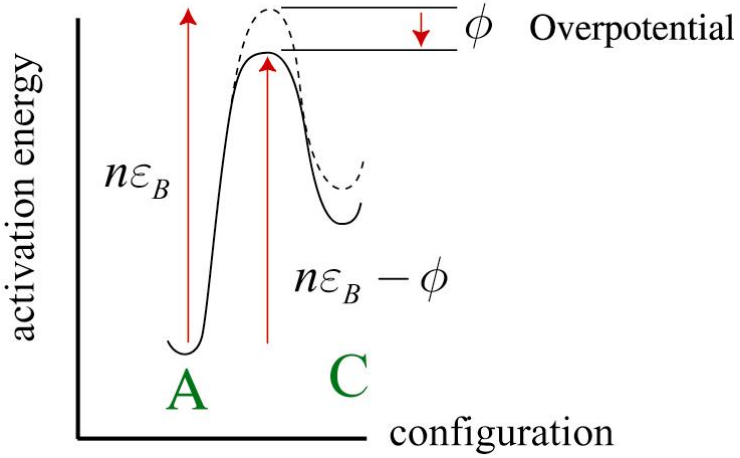
*bond breaking model*




*Dissolution of Less Noble Species*

$$k_{A\to C} = \nu_E \exp\left[-\frac{(n\varepsilon_B - \phi)}{kT}\right]$$

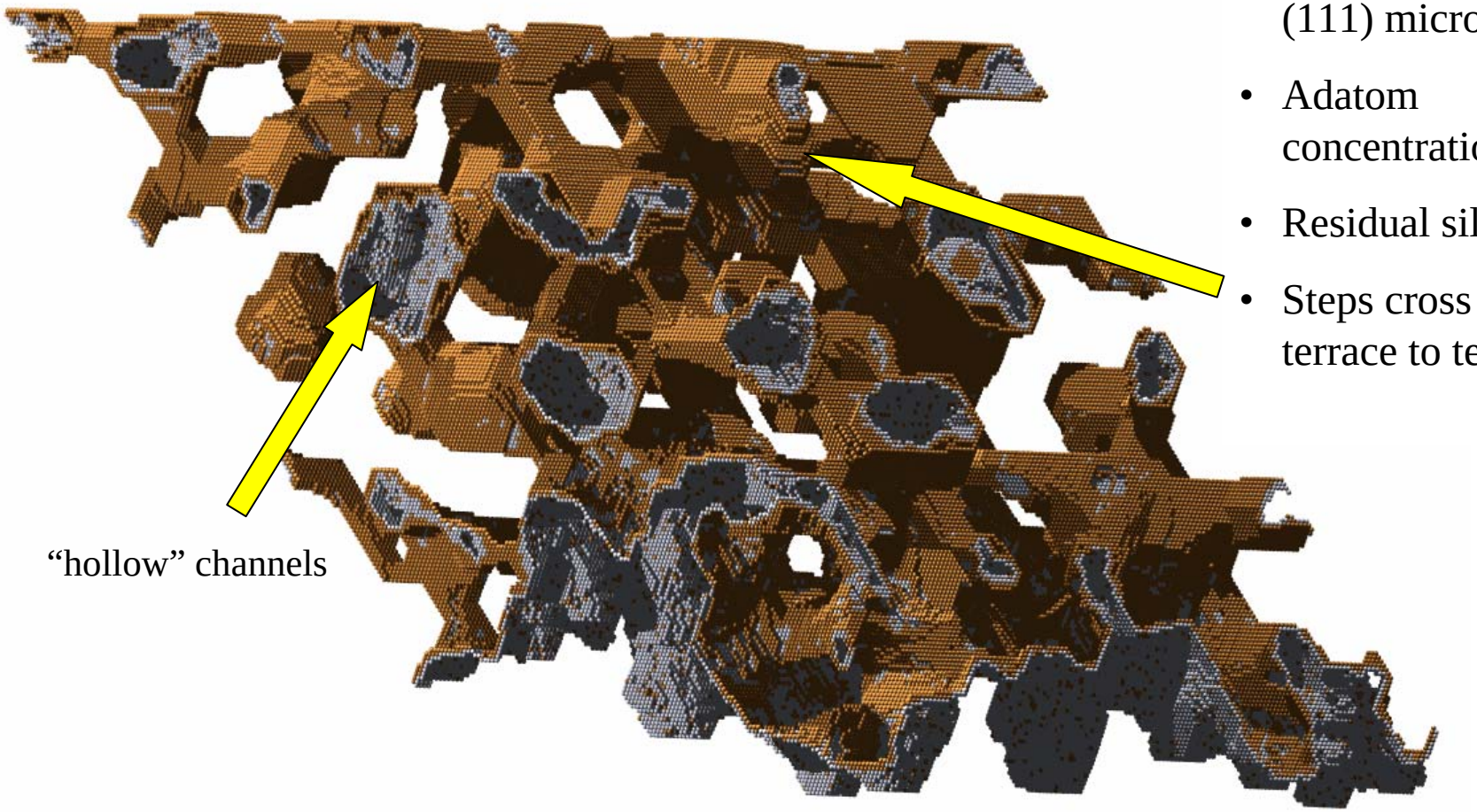
*consistent with the Butler-Volmer equation in electrochemistry*




Specific Values Used Here $\nu_D = 10^{12}\ \text{sec}^{-1}$ $\varepsilon_B = 0.285$ eV $\nu_E = 10^4 \text{sec}^{-1}$

$$\varepsilon_{Ag-Ag} = \varepsilon_{Au-Au} = \varepsilon_{Ag-Au} = \varepsilon_B$$

# Porosity Evolution: Dissolution >> Surface Diffusion

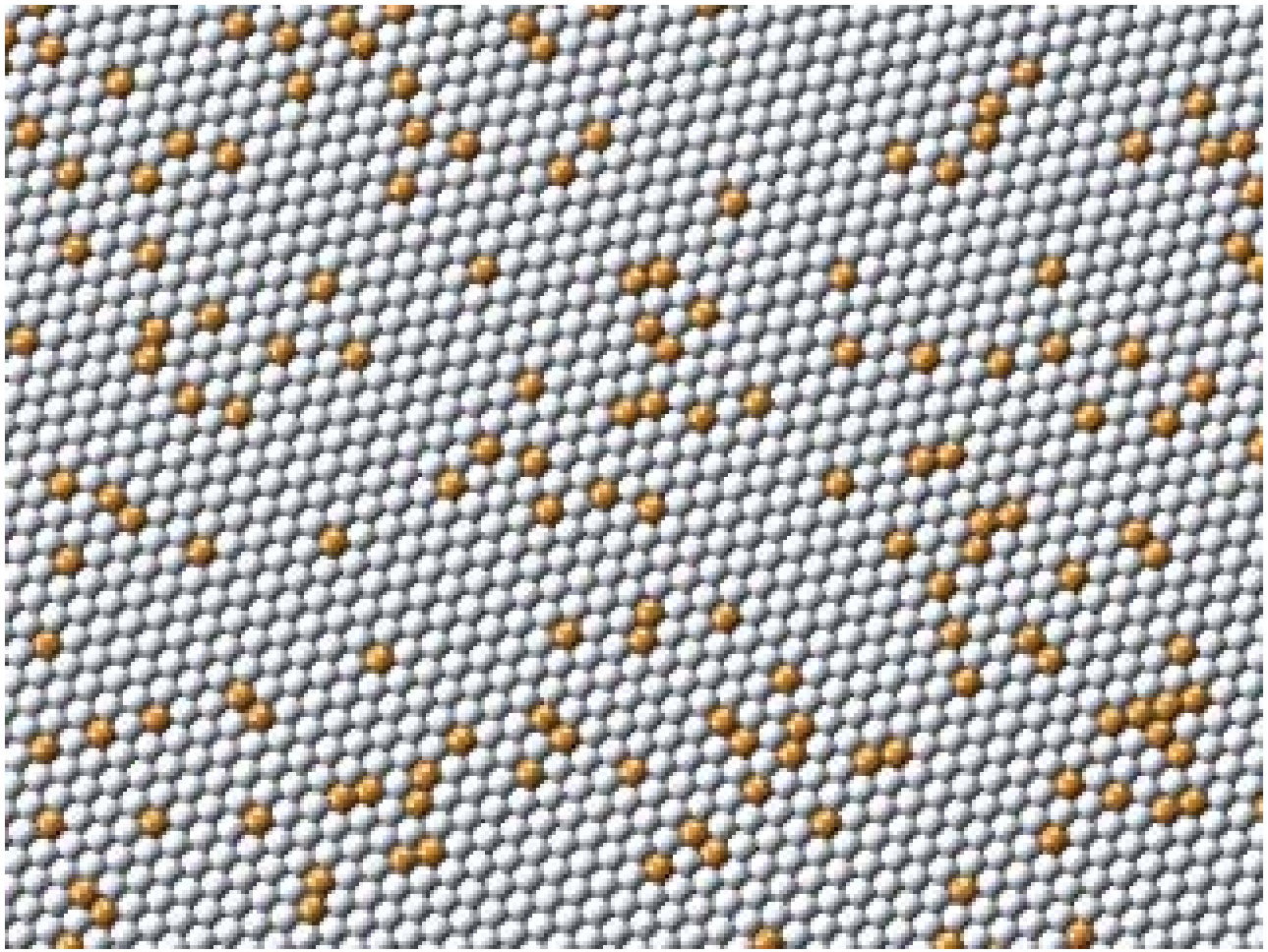


“hollow” channels

**Predictions**

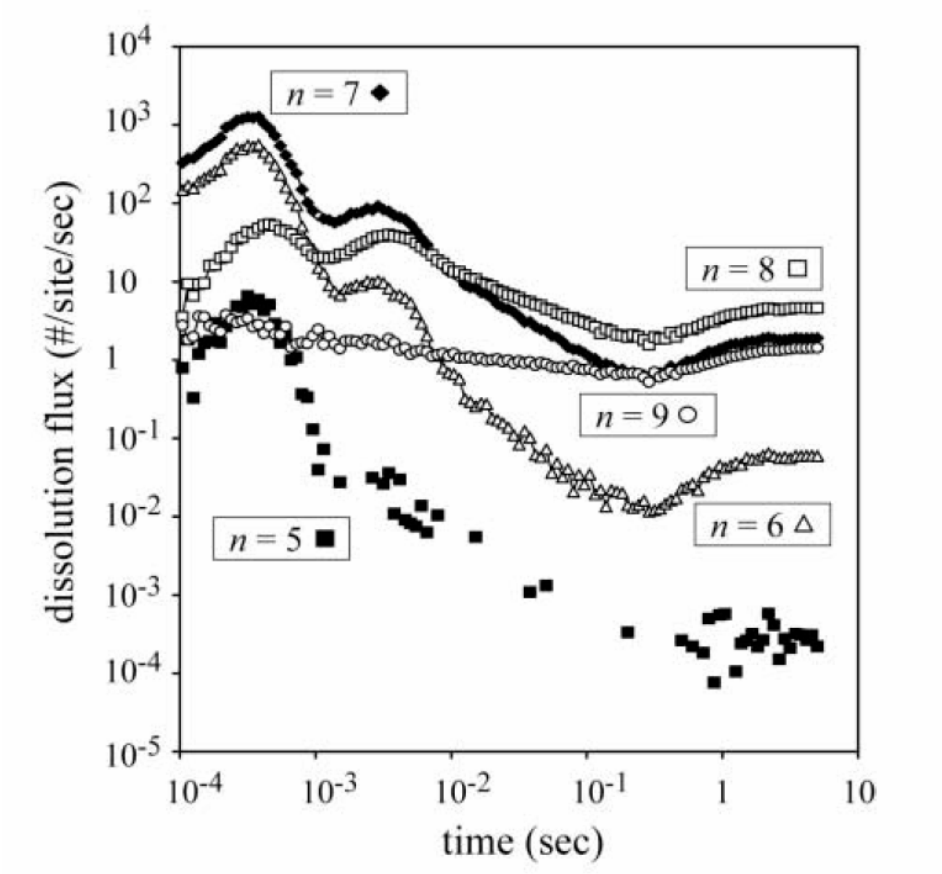
- NPG is essentially (111) microfaceted
- Adatom concentration is low
- Residual silver
- Steps cross from terrace to terrace

# Porosity Evolution: Dissolution >> Surface Diffusion



*Mobility of gold atoms is really step mobility*

# Coarsening of NPG




**What is the nature of coarsening?**

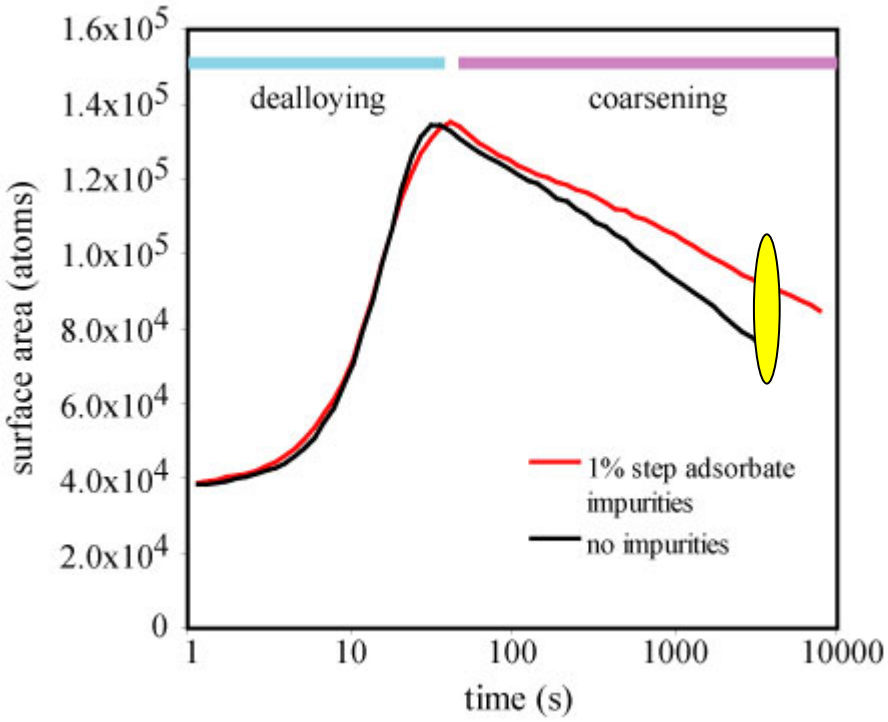
- Adatoms moving from step to step across terraces?
- Are atoms moving along step edges from facet to facet?

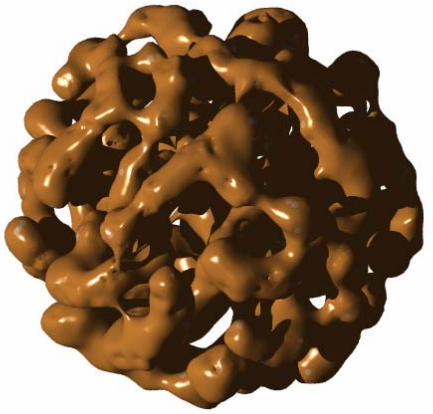
Contribution of n-coordinated atoms to the dissolution flux. Note: no *n*=3 atoms (adatoms)

Smaller pore sizes will result if step mobility is reduced due to impurities that pin step edges.

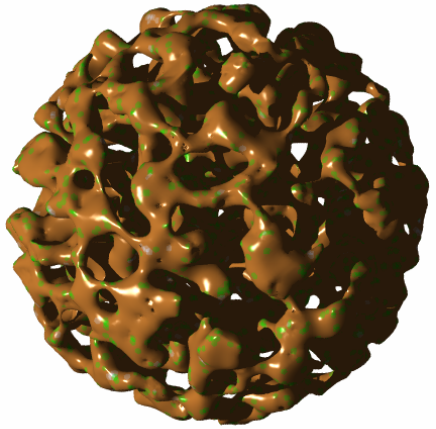
# Effect of Impurities on Coarsening of NPG: 1%

Model: add small % of impurity that likes step edges (i.e., strongly binds to gold)



*t* = 3000 sec

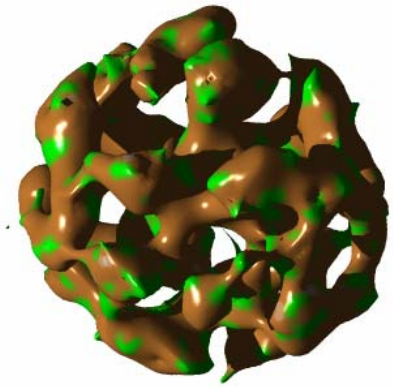


Ancillary problem: 1% aresenic in brass prevents dealloying

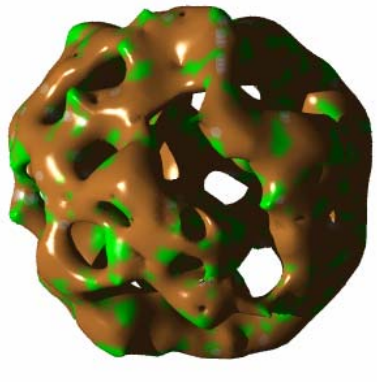
# Dealloying “30% Au- 65% Ag- 5% Pt”

Ag, Au are both only moderately miscible with Pt (solubility limit < 10%), with virtually no solubility of Ag, Au in Pt.

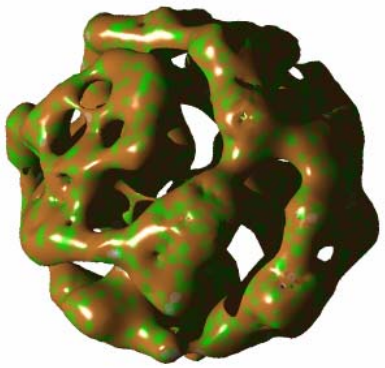
Model: $E_b$ = 0.15 eV Ag-Ag, Au-Au, Ag-Au
$E_b$ = 0.25 eV Pt-Pt



$E_b$ = 0.1 eV Ag-Pt, Au-Pt
1000 sec



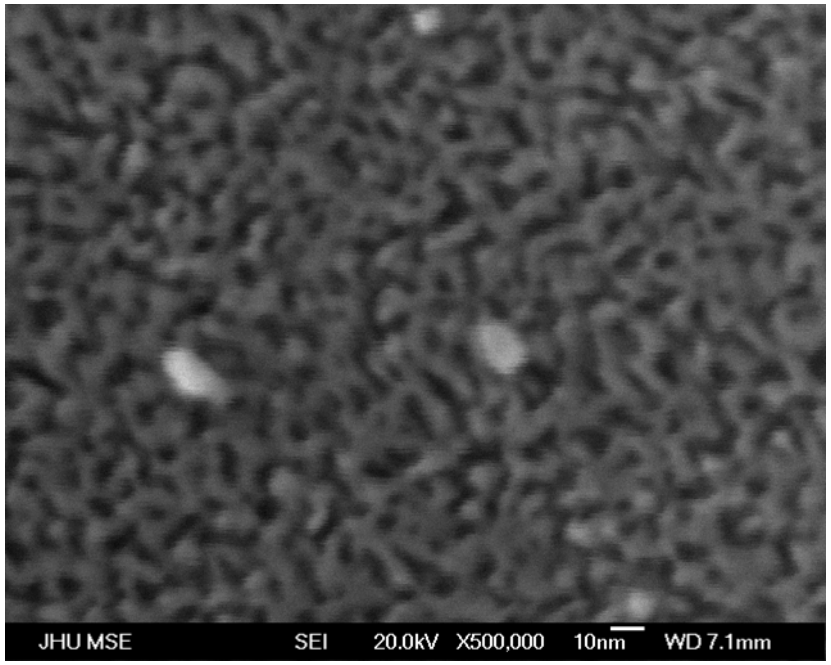
$E_b$ = 0.15 eV Ag-Pt
$E_b$ = 0.1 eV Au-Pt
1000 sec



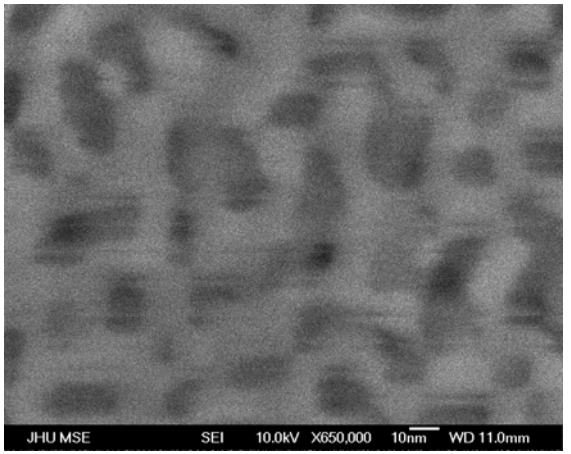
$E_b$ = 0.15 eV Ag-Pt
$E_b$ = 0.15 eV Au-Pt
1000 sec “control”

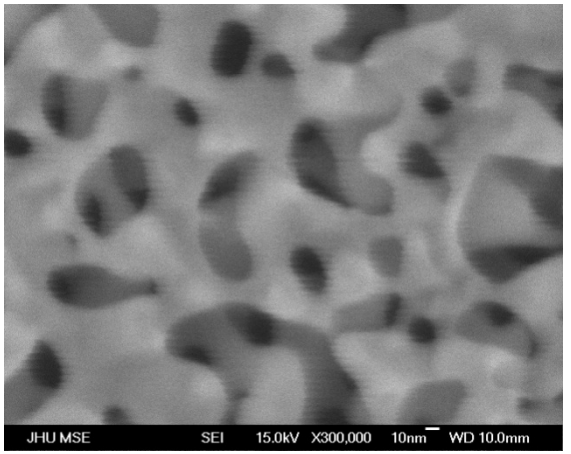
More Pt → smaller, more stable pores

# Dealloying *Real* 30% Au- 64% Ag- 6% Pt




- Electrochemically annealed in concentrated nitric acid, 24 hrs
- Pore size is < 5 nm!




NPG for comparison:

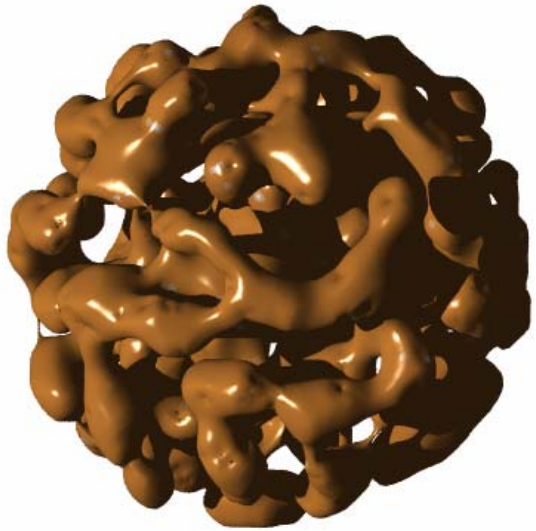
- as-formed (top)
- 24 hours in nitric acid (bottom)

# Conclusions

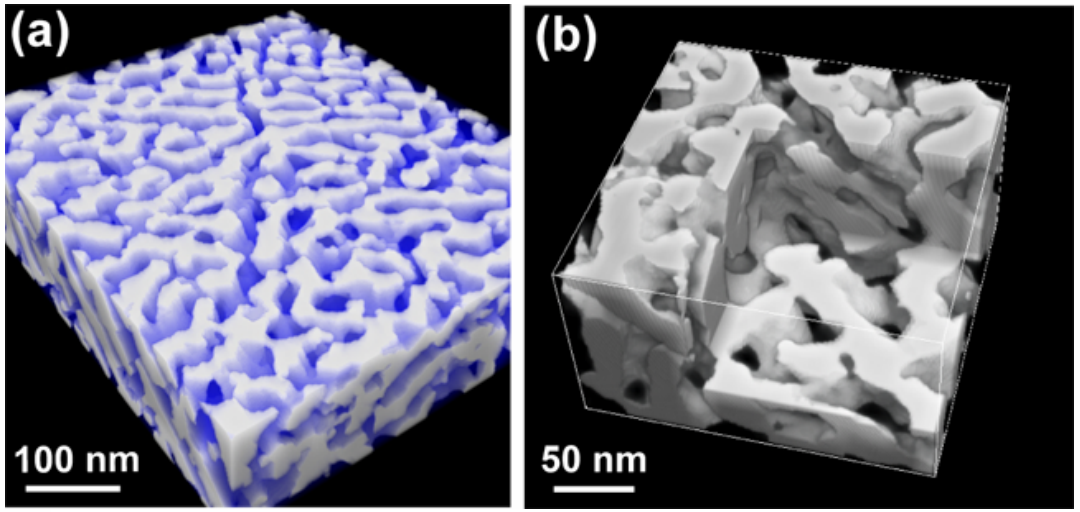
- KMC simulations give useful insights into porosity evolution
- Pinning of step edges may lead to smaller scale features sizes
- Adding impurities both shrinks pore size and segregates “impurities” to surface

*Thanks!*

# Reality vs. Simulation

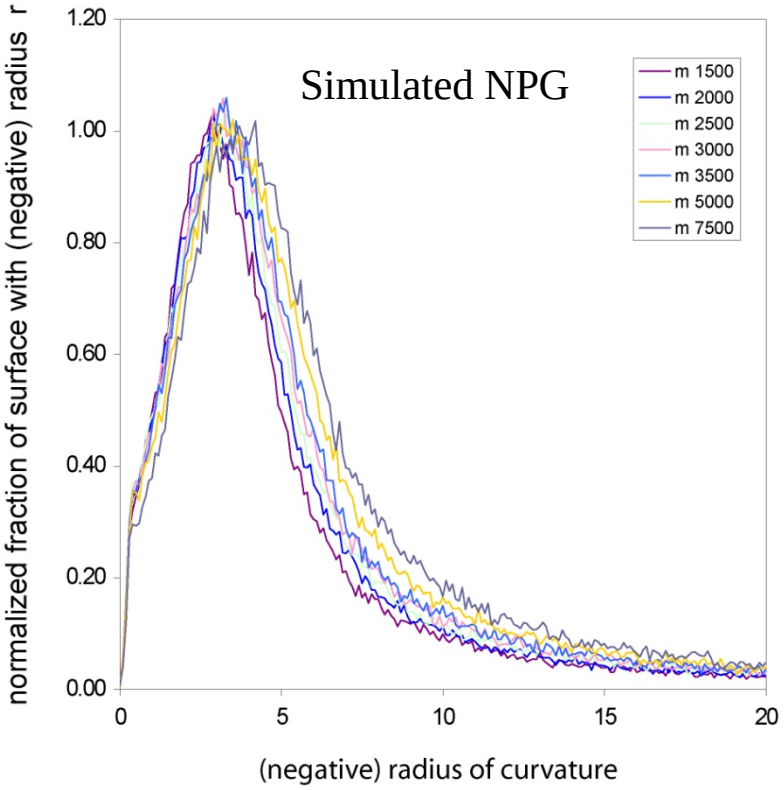


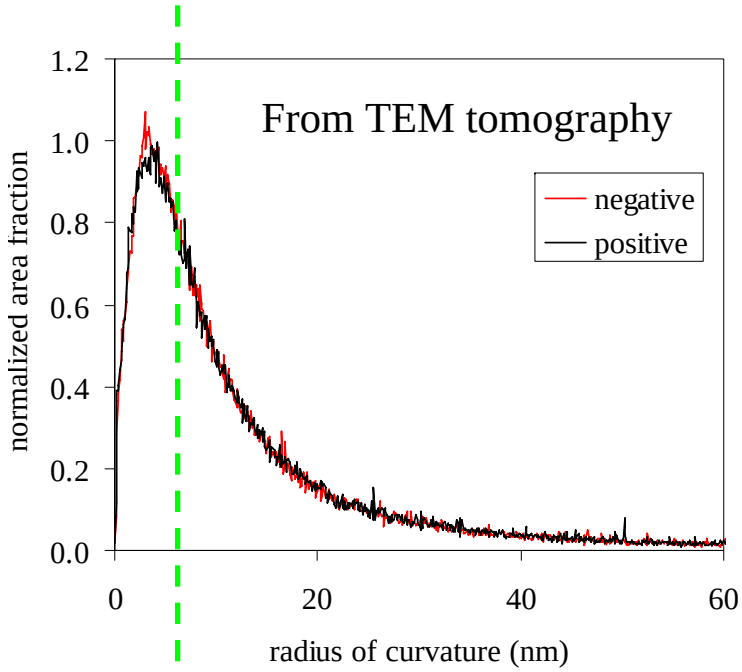
Simulated NPG




TEM tomography of NPG (with M. Chen, T. Fujita)

# Detailed Morphological Characterization of NPG




Median curvature = 7.5 nm

*Preliminary conclusions:*

- NPG really does coarsen self-similarly
- Surface is close to a net “zero-curvature” morphology