Sub-Nanostructured Non-Transition Metal Complex Grids for Hydrogen Storage

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May 23, 2005

Project ID # ST7

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Project start date: 1/20/04 (contractual)
  April 2004 (actual)
- Project end date: 1/19/07
- Percent Completed: 30 %

Budget

- Project funding: $1,201,862
  - DOE share: $ 959,317
  - Contractor share: $ 242,545
- Funding received in FY04: $ 310,407
- Funding for FY05: $ 190,000

Overview (con.)

- **DOE On-Board Hydrogen Storage Barriers**
  -C. Efficiency
  -D. Durability
  -E. Refueling Time
  -M. Hydrogen Capacity and Reversibility
  -N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Partners

- Steven M. Kuznicki, U. of Alberta; zeolite chemistry
- Suha Yazici, Graftec; electrochemistry
- David Sholl, Carnegie Mellon U.; computational (pending)

OBJECTIVE

- To develop the techniques to make nanostructured continuous three-dimensional metal alloy grid for hydrogen storage
- To make and characterize the grids for state-of-art alloys

TECHNICAL APPROACH

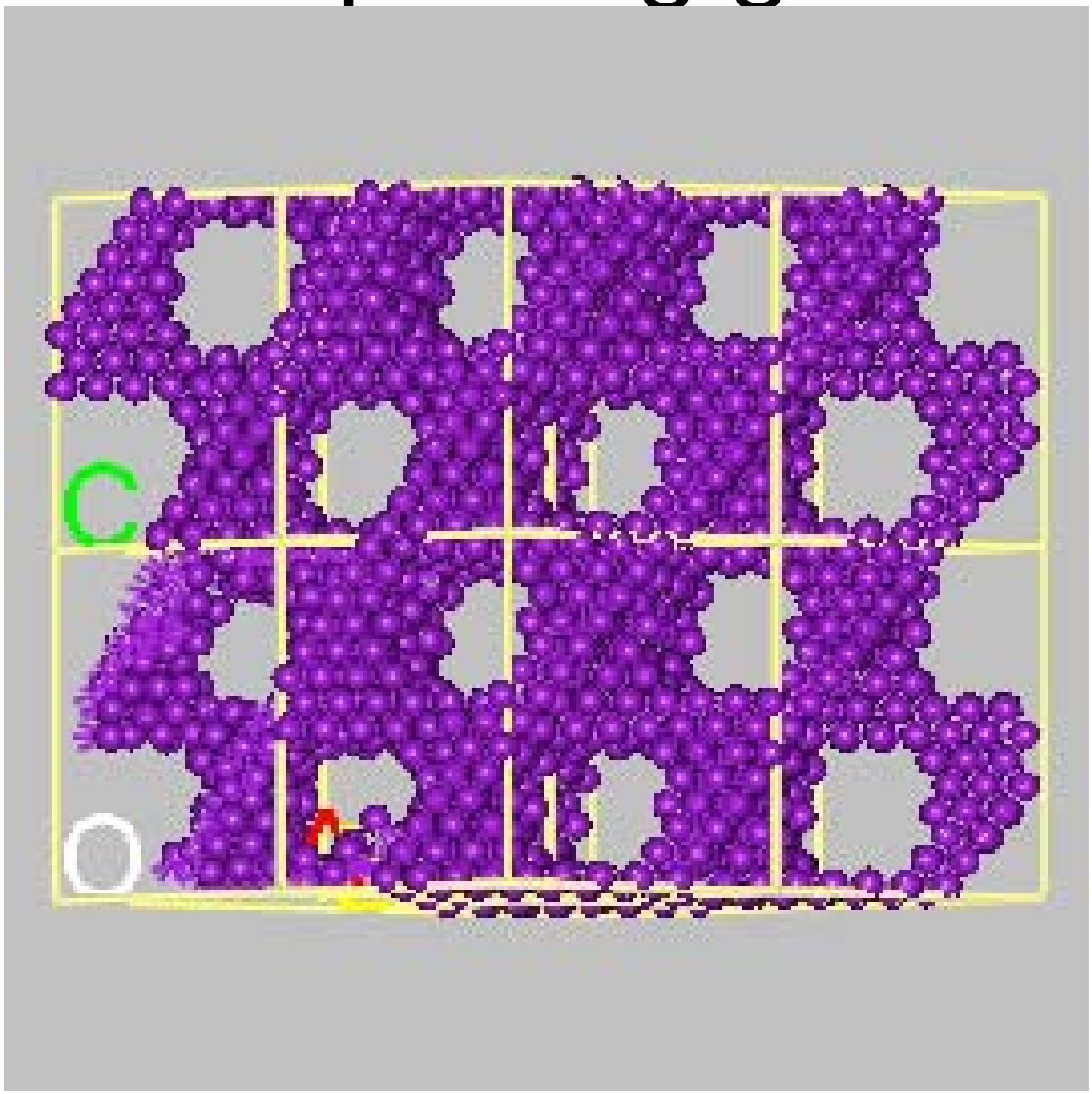
1. Use nanoporous (e.g. zeolite) templates as mold on cathode
2. Electrodeposit metals in the pores to grow nanostructured grids
3. Dissolve the mold and recover the metal grid

WHY NANOSTRUCTURE ?

- Large surface area increase H_2 dissociation rate
- Smaller diffusion distance increase H-transport rate in metal
- Flexible/open structure decrease decrepitation by cycling
- Energy release/absorption & mass/energy transfer throughout matrix improve heat transfer characteristics
- Large surface area increase storage capacity by physical adsorption
- Possible Increase in capacity by quantum effects ? (30-50 atom clusters)

Increase dynamic hydrogen uptake !

Example: Mg grown in faujisite



Cubic superlattice;
a=2.4 nm

Characteristic length (pore or solid);
L = 1nm

Porosity;
$\varepsilon = 0.5$

Surface area;
$\tau = 500\ m^2/gm$

Expected improvements

Base case: 1 mm solid metal particle

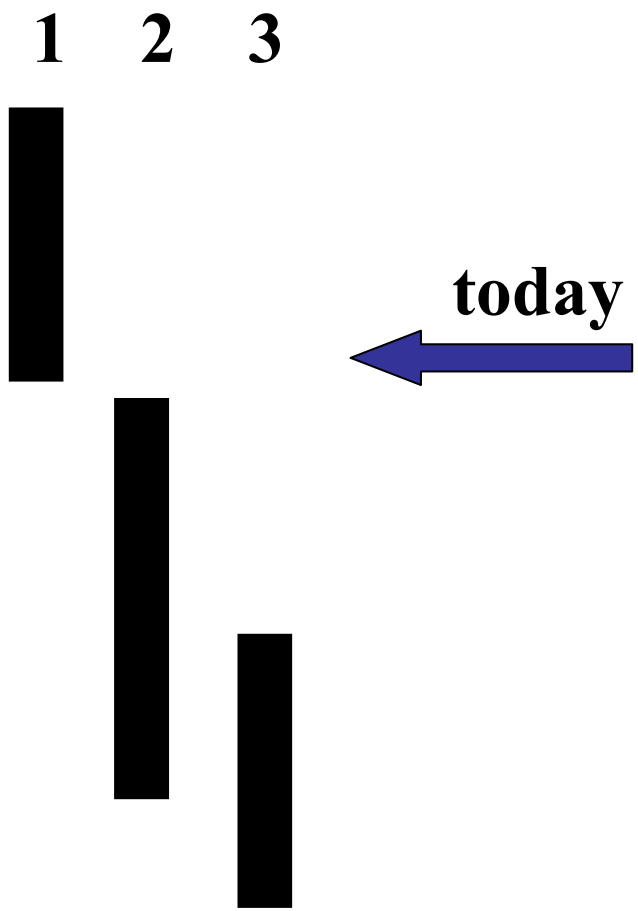
	Comment		Increase
H_2 dissociation rate	scales with 1/L		10^6
H diffusion rate	scales with ε/L		$0.5x10^6$
Energy flux in metal	$k(1-\varepsilon)\delta^2T/\delta x^2$ *conduction* **lower ε**	$(\varepsilon D\delta C/\delta x)*C_p\delta\Delta T/\delta x$ *(mass flux)*enthalpy* **additional, small**	$r^s(\Delta H+C_p\Delta T)$ *reaction* **additional, large**
Physical adsorption	Scales with 1/L		10^6

ISSUES/QUESTIONS

- Volumetric capacity reduced by a factor of ε compared to bulk metal

- Will the metal sinter during cycling?

TASKS



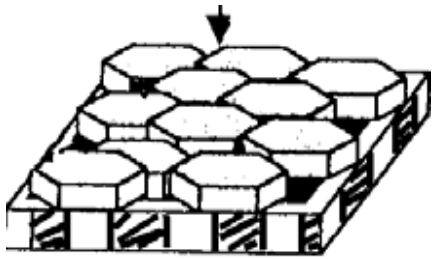
1. Mold/Cathode preparation
2. Pure metal electrodeposition
   characterizations
3. Mold removal, grid recovery
4. Pure metal hydrogen storage
5. Mixed metal electrodeposition
   characterizations
6. Mixed metal hydrogen storage

TASK 1: Mold/Cathode Fabrication

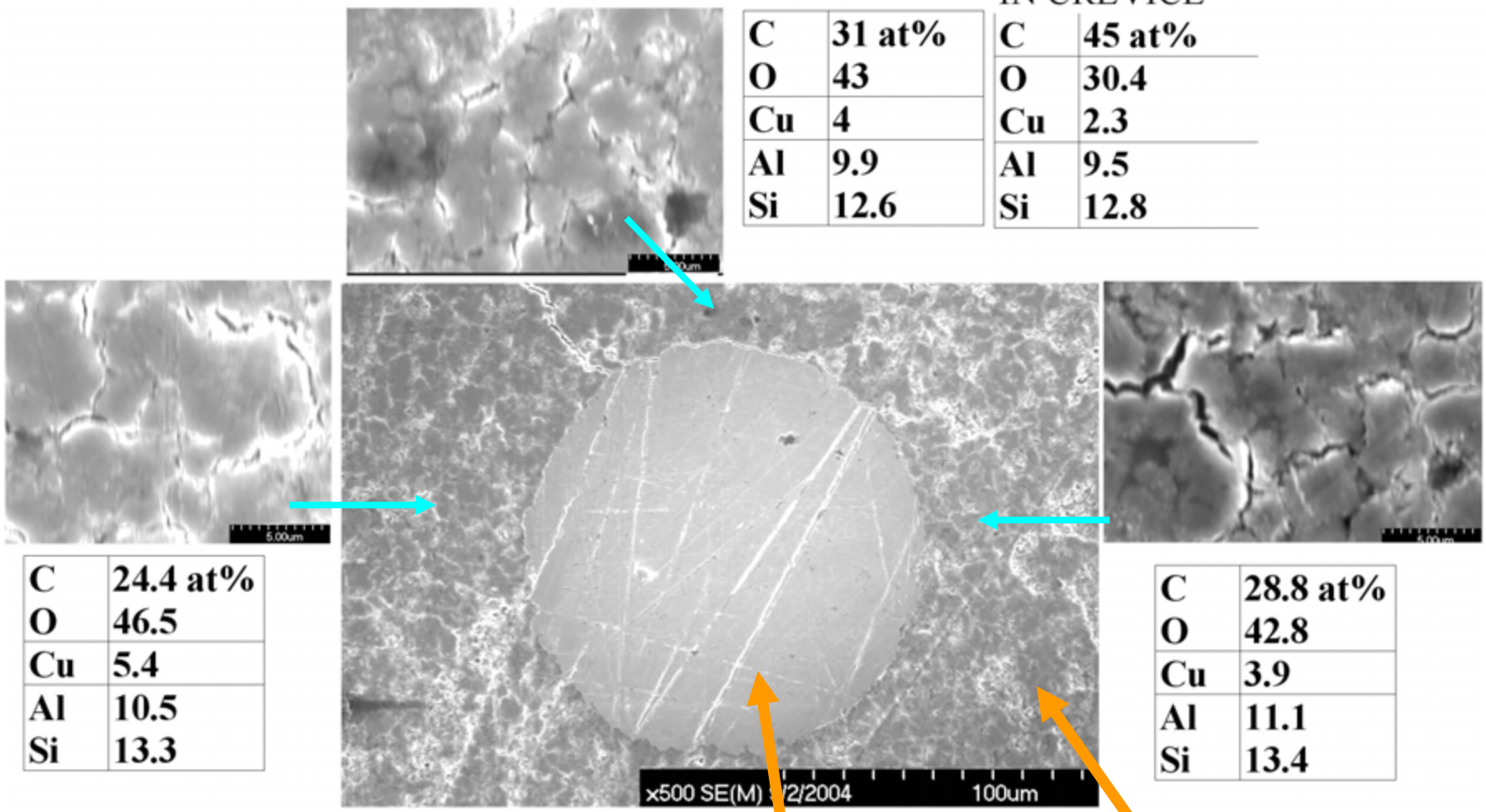
Least Attractive

1. Multicrystal particles compacted on a metallic substrate.
2. Multicrystal film of inter-grown crystals in-situ synthesized on a metallic substrate.
3. Multicrystal film containing large oriented crystals grown on a metallic substrate.
4. Very large single nanoporous crystal grown on a metallic substrate ?

Most Attractive



Electrodeposition in compacted powder



TASK 1.1 Compaction Summary

•Faujisite powder (Si/Al=1.4, 1 μm particle) exchanged to Cu compacted on Ni mesh used as cathode

•Cu electrodeposited in the pores

•EDX shows Cu enrichment in zeolite crystals

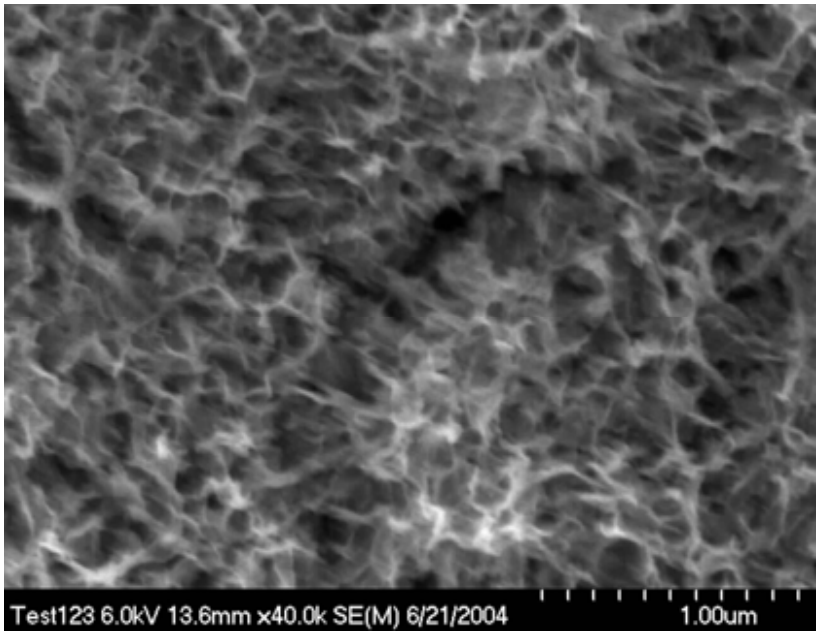
•Cu/Al ratios: 0.51 left (closest to anode), 0.4 top, 0.35 right

•excessive Cu growth in between zeolite particles (like tree roots in stony soil)

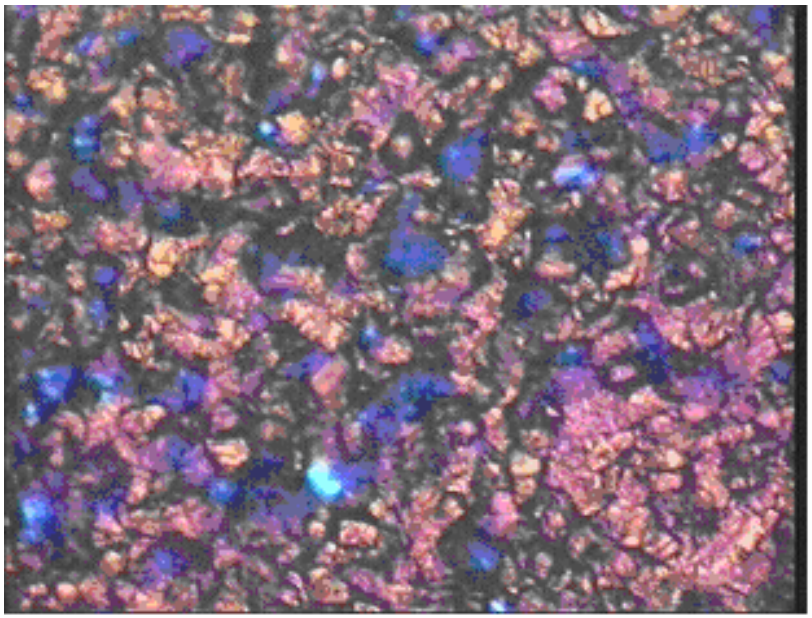
➢ ***electrodeposition in zeolite particles works***

➢ ***hard to prevent growth in between particles***

Anodized Ti-cathode for in-situ growth

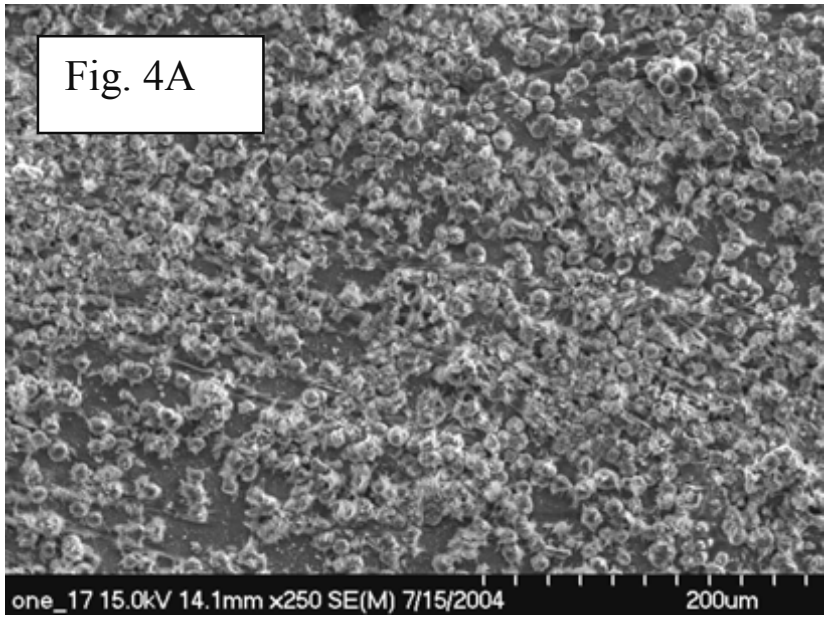


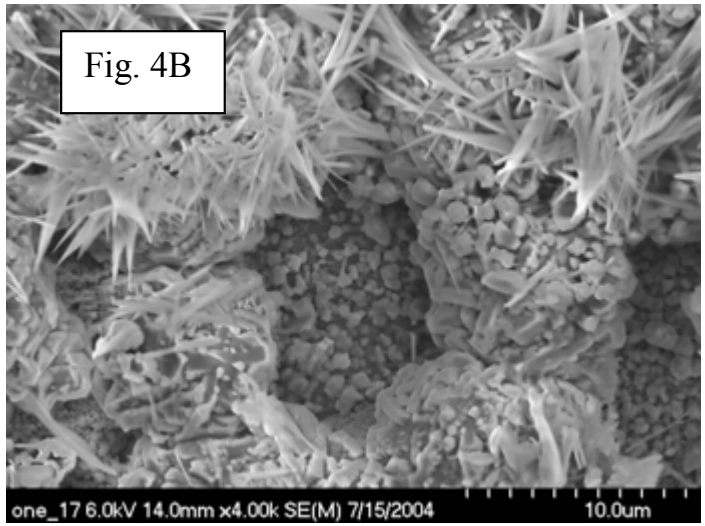
- NaOH treatment at 60 C, cure at 500 C
- TiO_2 is formed (anatase)
- Ti metal is also exposed
- Texture 0.1 to 10 μm, controlled by treatment conditions (0.1 μm shown)



- Purple = TiO_2 (for adhesion of zeolite)
- Blue = Ti metal (for electrical conductivity)

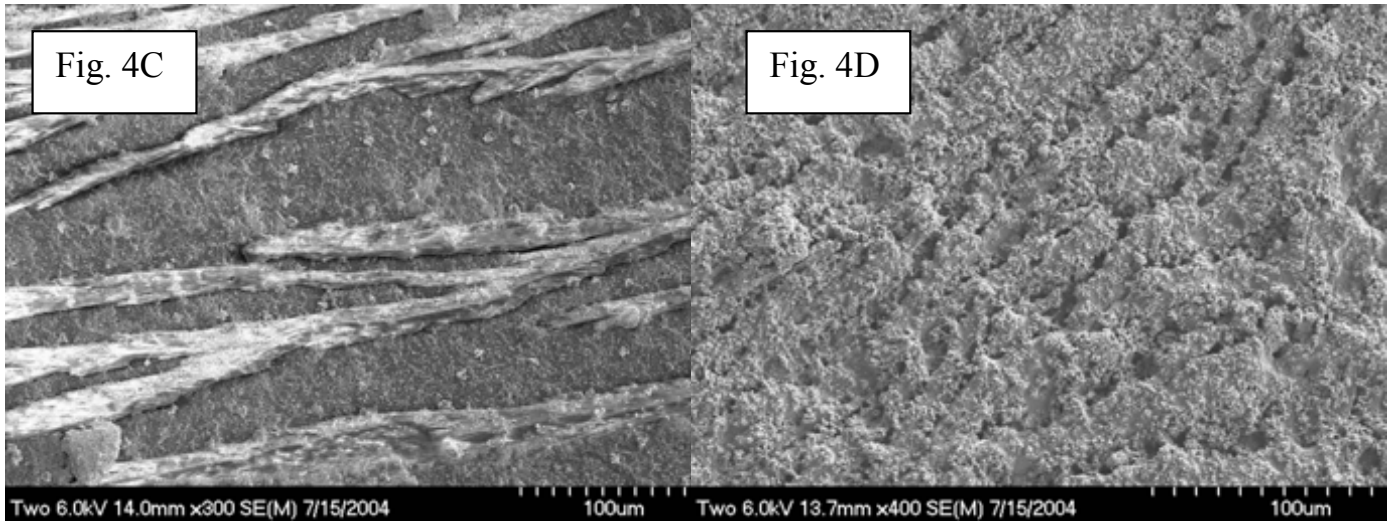
Faujisite growths on anodized-Ti





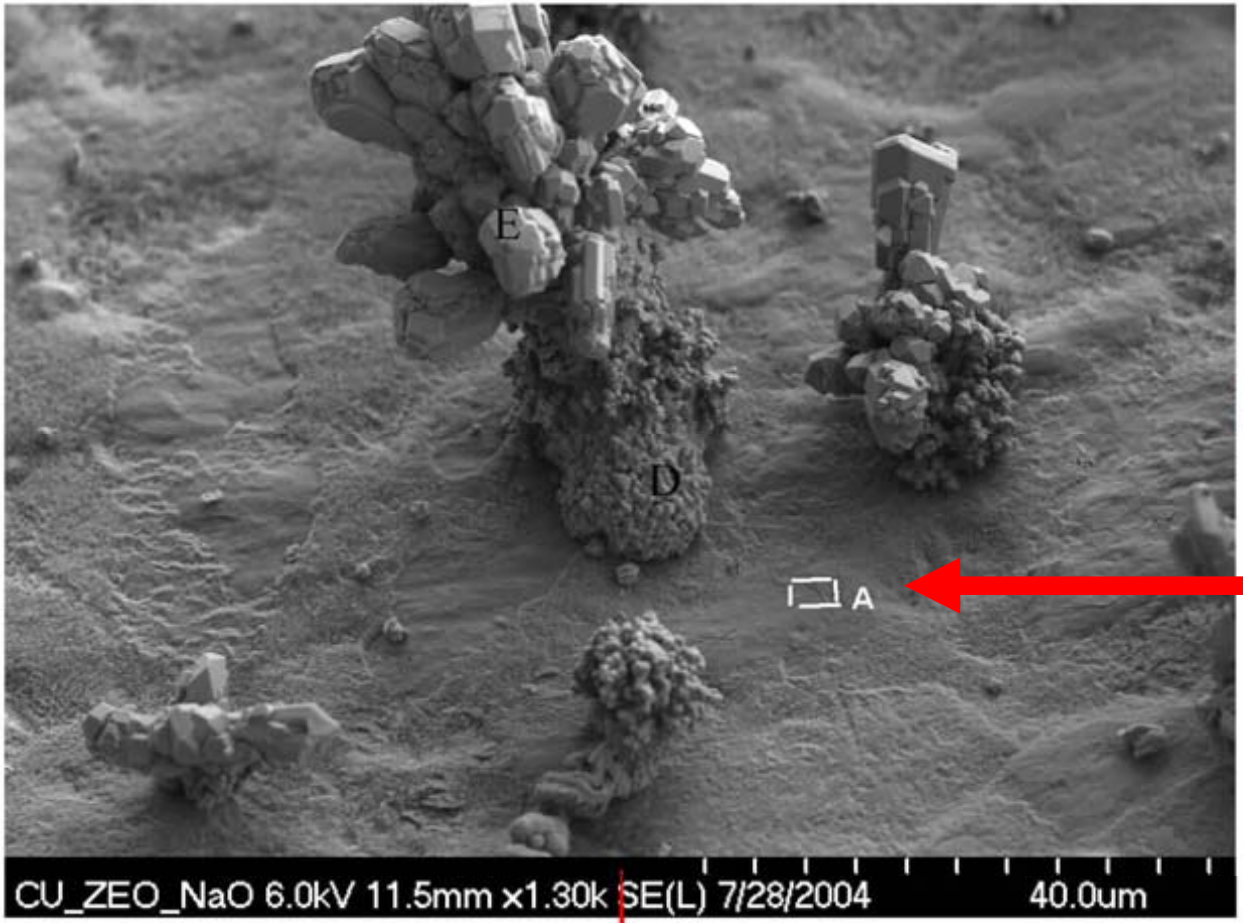
Same chemistry, different magnification

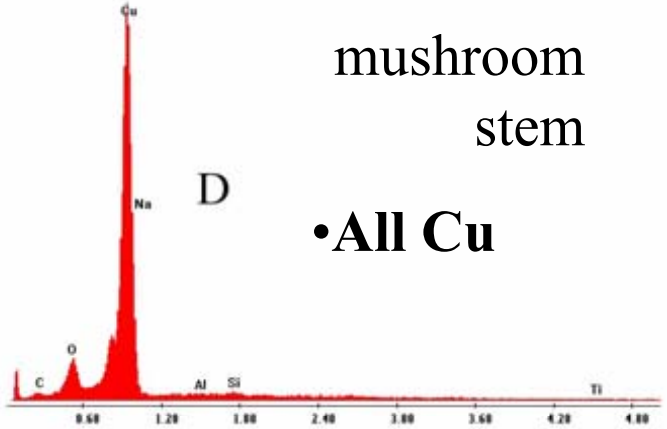
Two other chemistry's



picked the best adhesion chemistry for electrodeposition

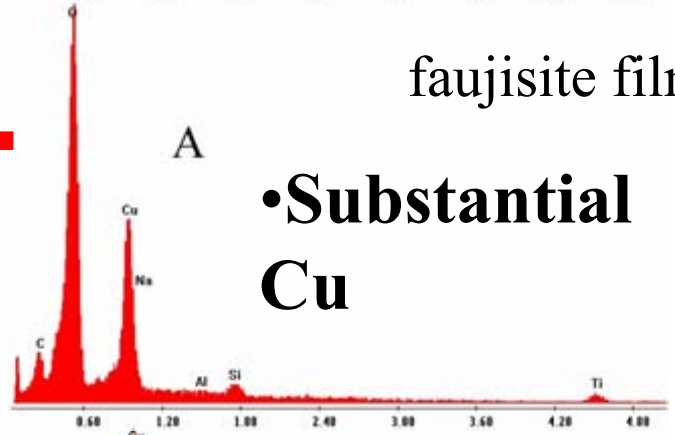
Electrodeposition in synthesized zeolite film





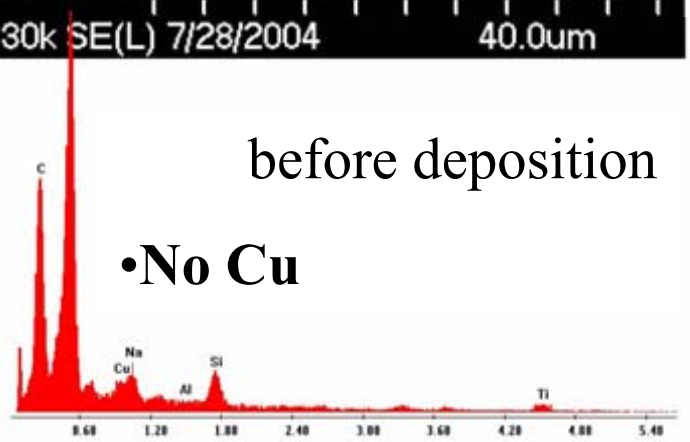
mushroom stem

- **All Cu**



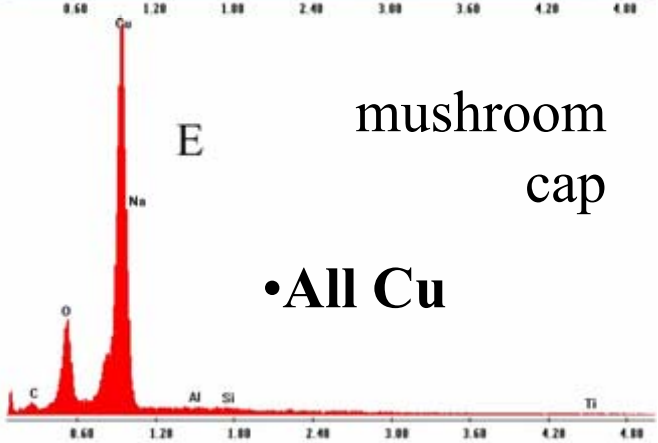
faujisite film

- **Substantial Cu**



before deposition

- **No Cu**



mushroom cap

- **All Cu**

Task 1.2 Anodized Ti + Faujisite + Cu-deposition

- Metal (Ti) is microstructured to TiO_2 to promote zeolite film growth with good adhesion
- Cu is electrodeposited in zeolite pores

- ***No Cu growth between particles***
- ***"mushroom" overgrowth will be prevented***
- ***Need to grow thicker films***
- ***Try also anodized aluminum***

TASK 2: Electrodeposition

•Vast electroplating/electrodeposition literature is primarily geared to optimize the uniformity[1] of thin films[2] on large smooth[3] cathode surfaces of a different[4] metal.

•We are trying to deposit non-uniform[1], "thick" bulk[2] metal in small nanopores[3] of a non-conducting material. (The cathode/anode conductor can be the same[4] metal.)

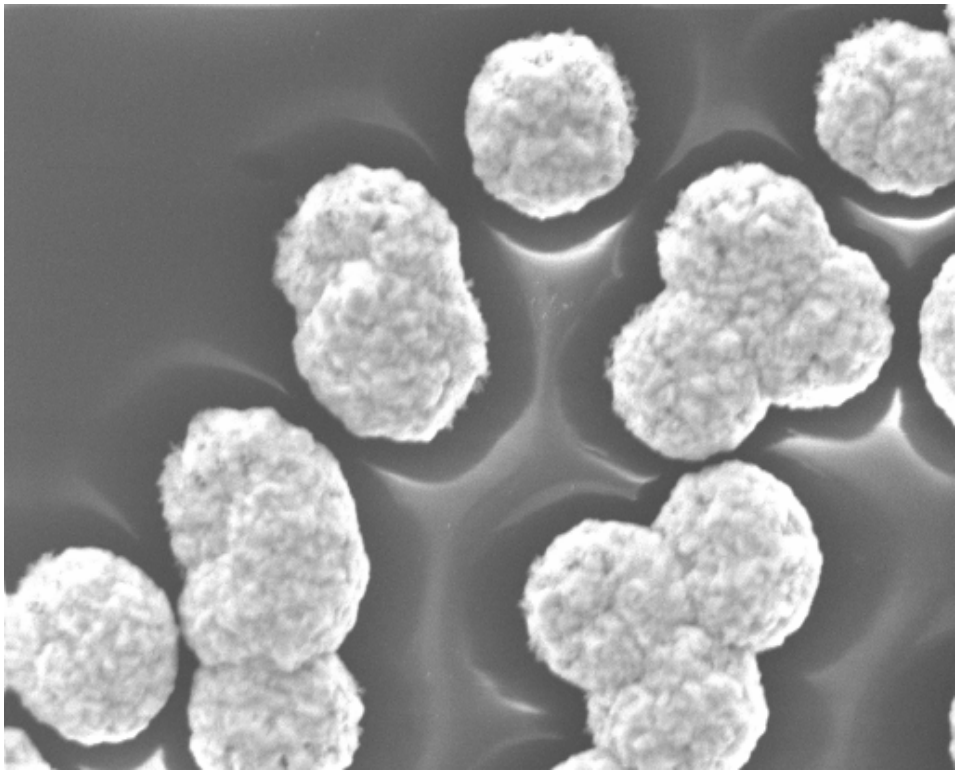
Need to fine-tune electrodeposition at nano-scale.

Electrodeposition in track-etched polycarbonate films (PCF)

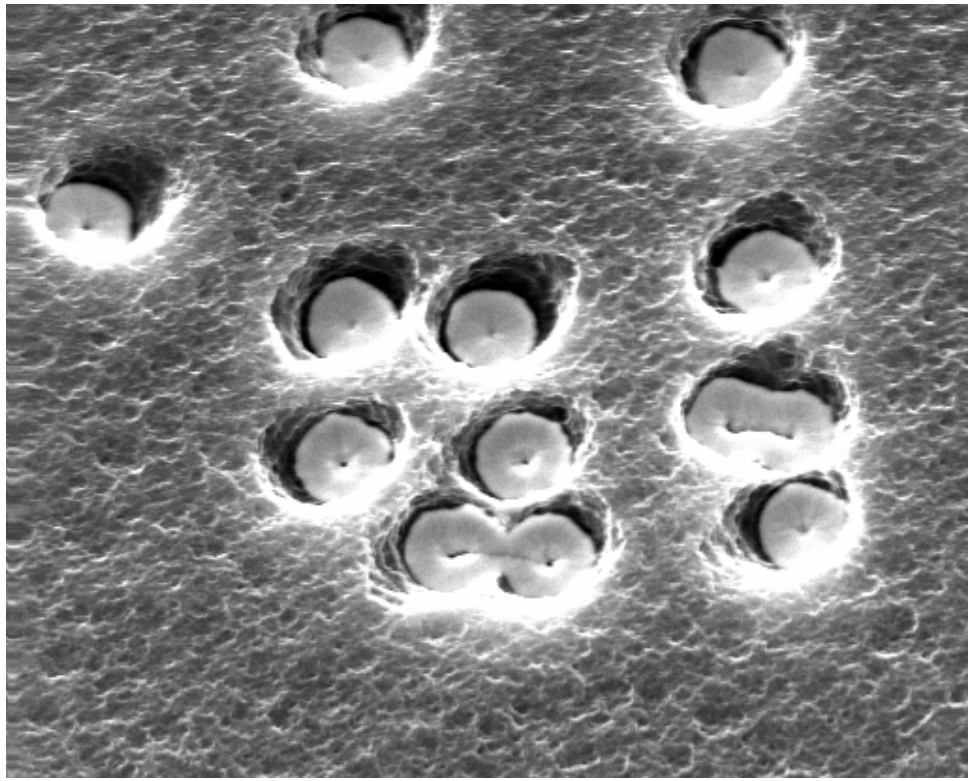
- Commercially available membranes used as cathode mold
- Non-conducting polycarbonate "mold" (like zeolites)
- Pore sizes from 1 μm, down to 0.015 μm = 15 nm (150x larger than zeolite pores, hard to scale)
- Film thickness up to 10 μm (zeolite crystal size, close scale)
- Porosity up to 10% (less than zeolites, easy to scale)

Analyze effects of electrolyte chemistry, deposition conditions, and mold characteristics for electrodeposition at nanoscale

Cu deposit in 10 μm holes of PCF



Solution side at 1,000x



Cathode conductor side at 1,000x

Caps coalesce, diameter closer to 10 μm

No growth on Au coating

Holes in center of deposited Cu suggest inwards growth from walls

Task 2: Electrodeposition fine tuning

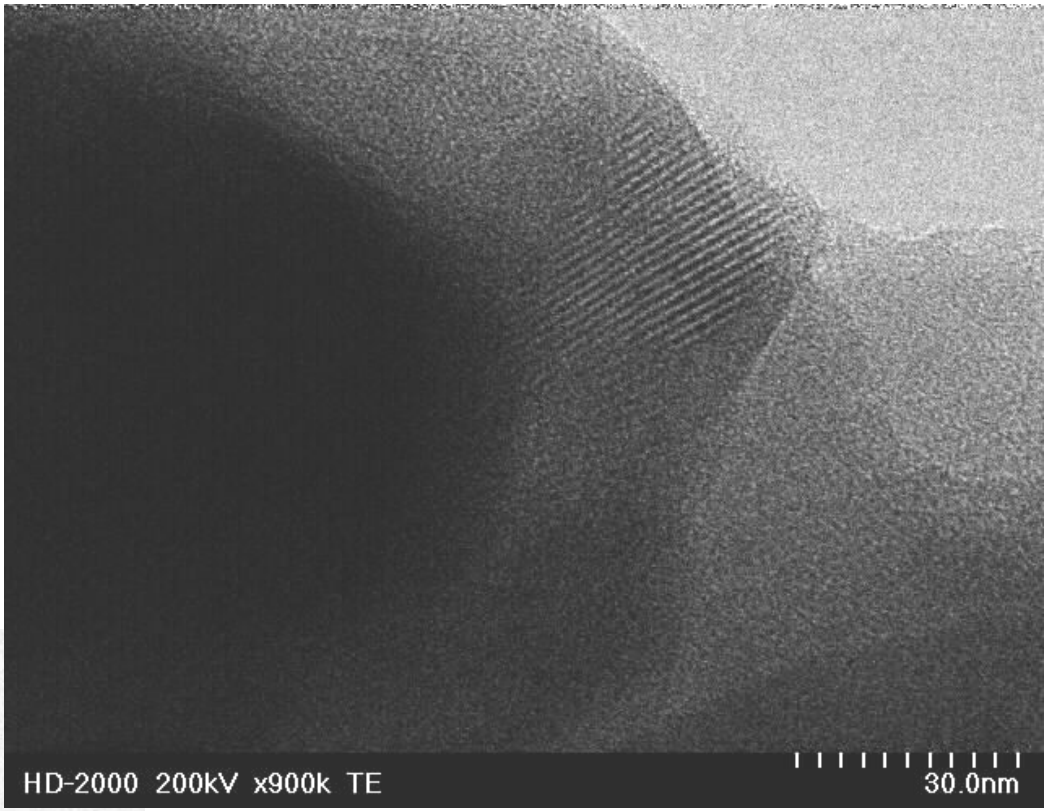
- PCF as "proxy" to fine tune electrodeposition parameters
- Identified controlling radial versus axial growth
- Significant effect of pore size

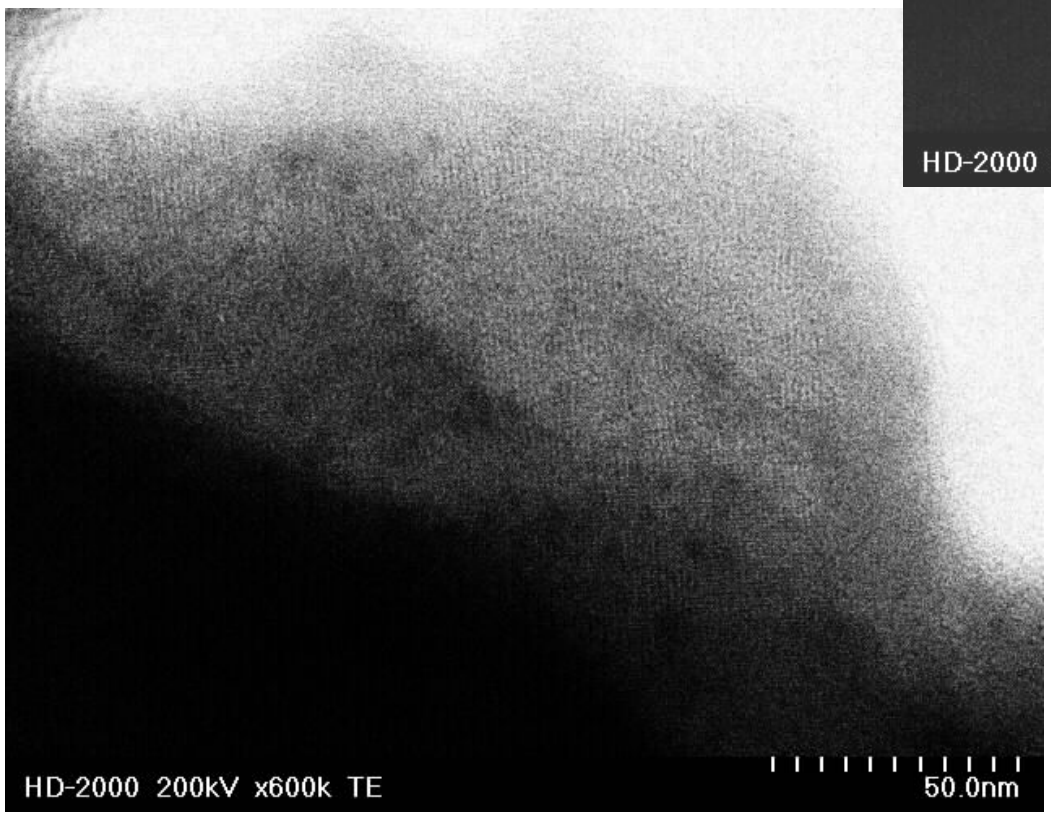
<u>Future</u>

- Extrapolate to nanoscale electro deposition (below 15 nm)
- Bring-in H_2 hydride electrochemistry

RESULTS

HRTEM images of faujisite after Cu electrodeposition



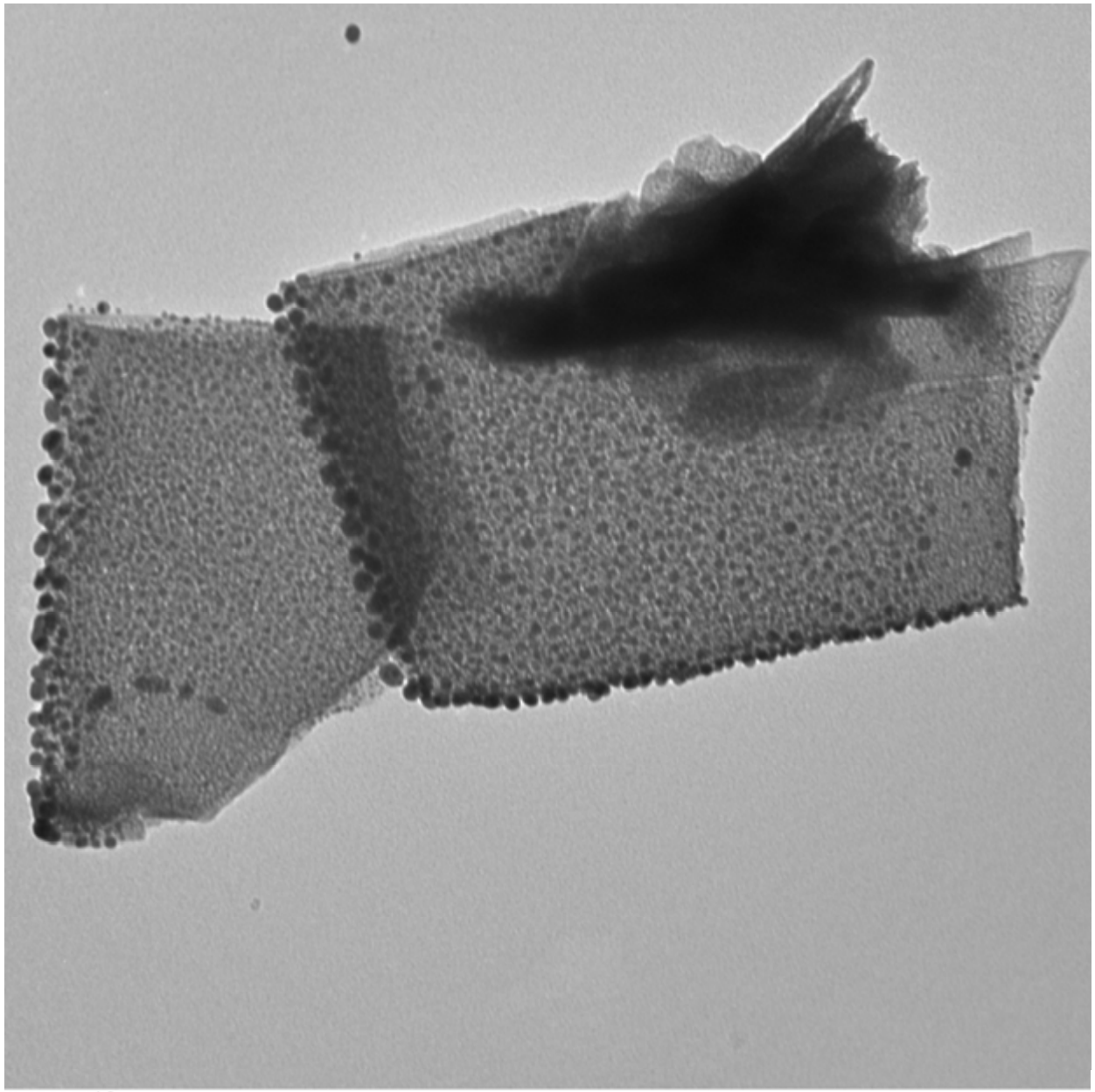


- 1 nm lines spaced at 1 nm
- No such lines in normal faujisite images

(Courtesy of Hitachi High Technologies America)

RESULTS

HRTEM of Cu “mushrooms” grown from nanometer pores



Next Year Activities

Remainder FY05:

- Multicrystal thicker zeolite grown on metals (Ti and Al)
- Oriented large crystal growth of nanoporous materials on cathodes
- Extrapolation of size effect on electrodeposition
- Switch from Cu to Pd (and Mg?) electrochemistry
- Characterization by HRTEM, STEM, AFM/STM, EDX

Next Year Activities (Con.)

FY06:

- Mold removal, grid recovery and surface area measurements
- Pure palladium (and magnesium?) for hydrogen storage testing
- Mixed metal electrodeposition chemistry

Auxiliary Slides

- Publications and Presentations

2 papers under review, 1 presentation scheduled for AIChE Annual meeting in Cincinnati, OH (Nov. 2005)

- The most significant hydrogen hazard associated with this project is:

The experiments to date did not require hydrogen. Limited uptake rate and equilibrium measurements will be performed in FY06 in our Rubotherm © magnetic suspension balance using small/lab quantities of H2 vented into fume-hood.

- Our approach to deal with this hazard is:

(Not applicable)