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Control of both particle and pore size in nanoporous Pd powders

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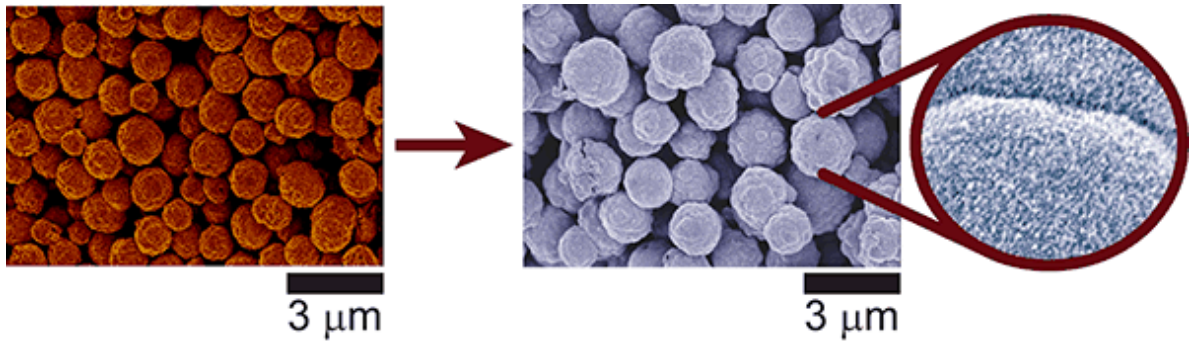

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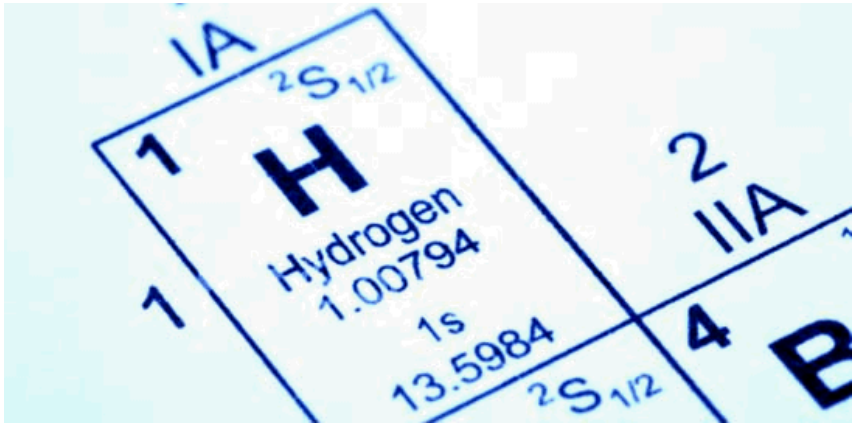
- Purpose
- Characteristics of Pd
- Advantages of nanoporous Palladium
- Synthesis Methods
- Copper as a Reducing Agent
- Materials analysis and Characterization
- Hydrogen Storage Capacity
- Optimizing Absorption Potential



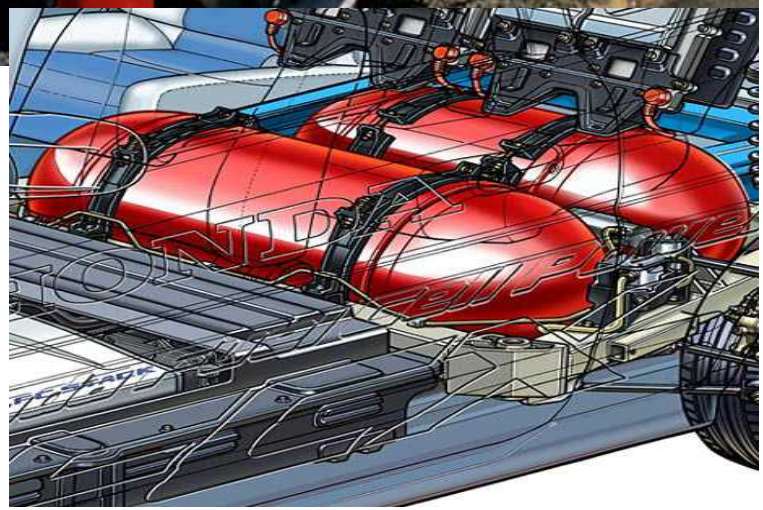
www.askipedia.com/wp-content/uploads/2012/06/hydrogen

www.sciencepicturecompany.com/images/4956/Palladium-Chemical-Element

Addressing Hydrogen Storage Limitations

- Current technology limited by storage capacity
- Gas storage systems require high pressures or low temp
- Solid state methods limited by transport rates between metal and hydride phases

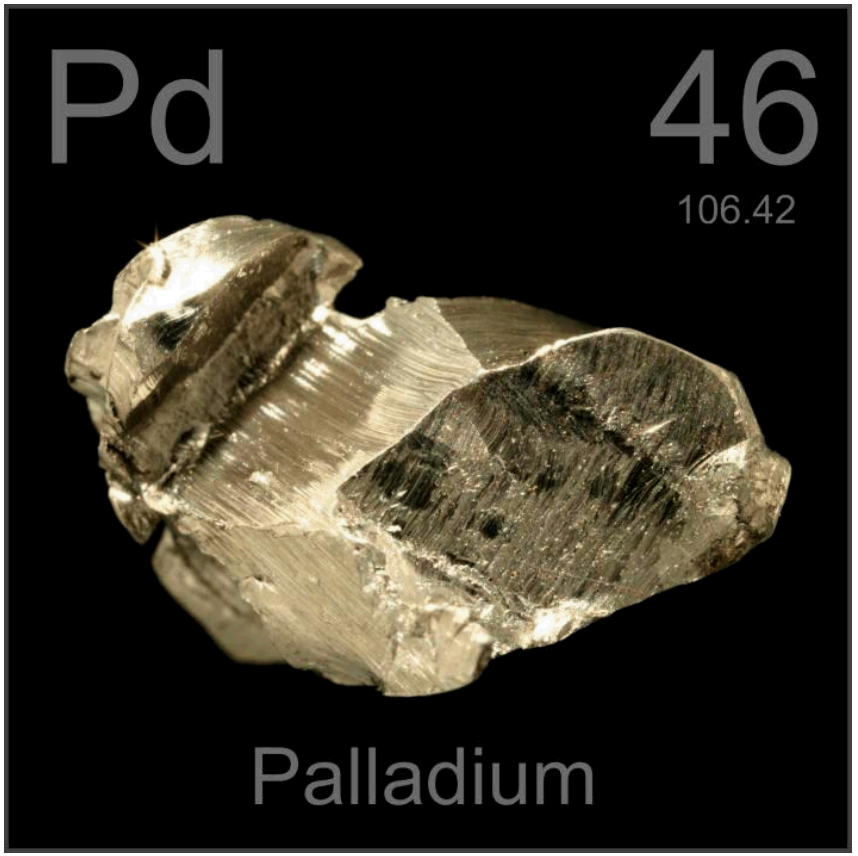
www.sri.com



www.pbs.org/wgbh/nova/sciencenow

Characteristics of Palladium

- Noble metal with low reactivity
- Ideal for solid state hydrogen storage
- Can absorb 900x its volume in Hydrogen
- Absorption rate limited by surface area
- Larger Surface Area = Faster transport rates



http://periodictable.com/Items/046.10/index.html

Advantages of Nanoporous Palladium

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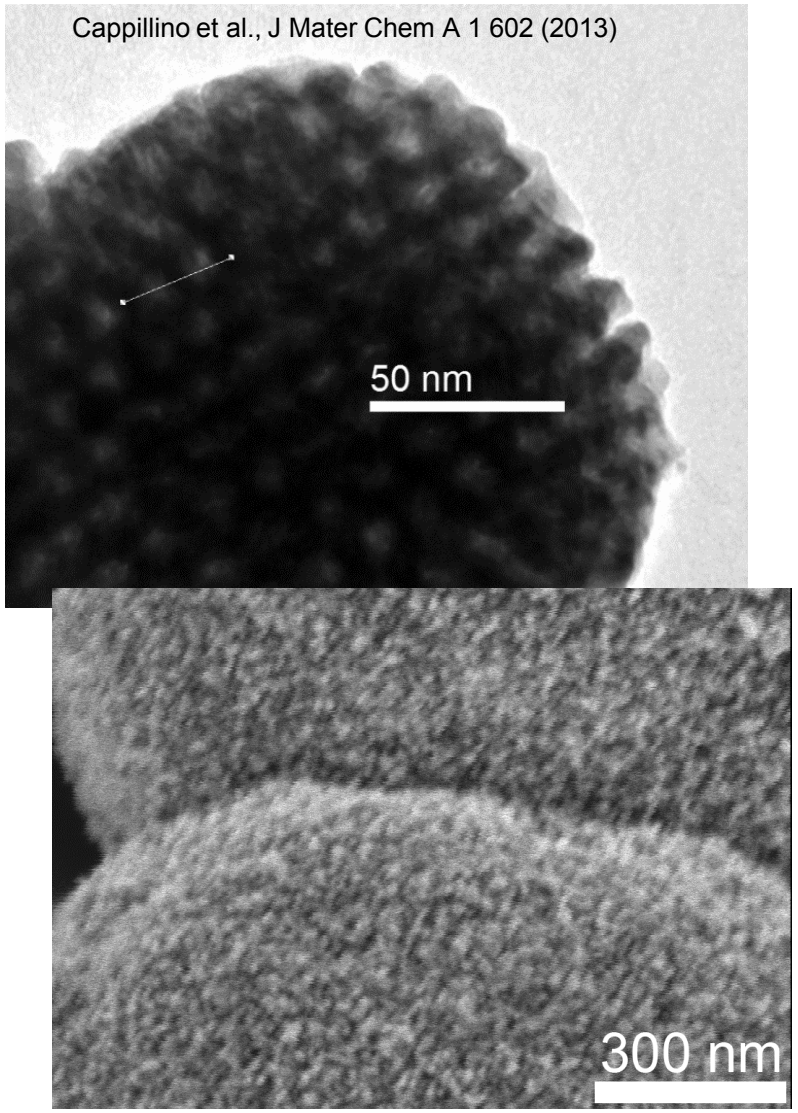
- Maximize surface area
- 10 – 20 nm diameter
- Pores = 100 atoms across
- Leads to faster reaction kinetics
- Pores help accommodate shrinking and swelling at electrode surfaces



Previous Work: Controlled pore size, but not particle size

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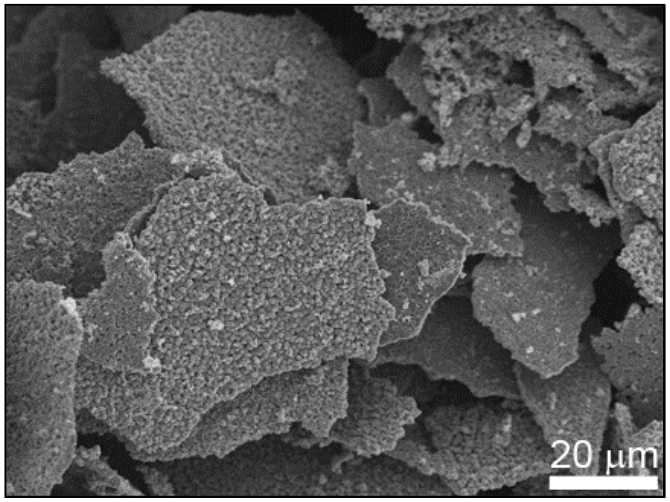
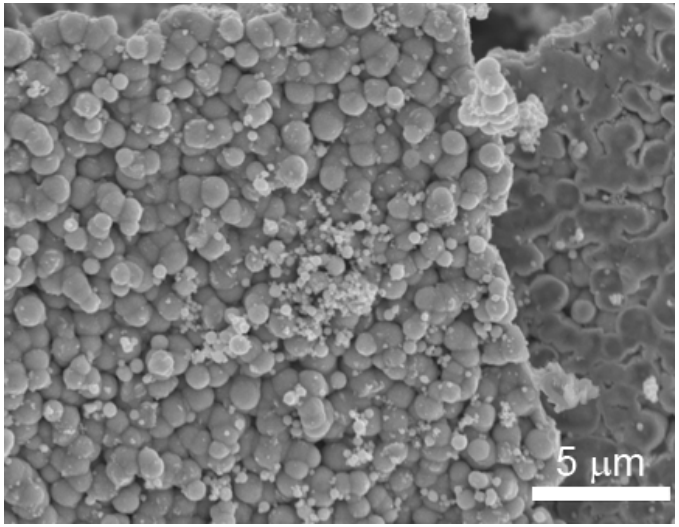
Irregular Particle Size/Shape



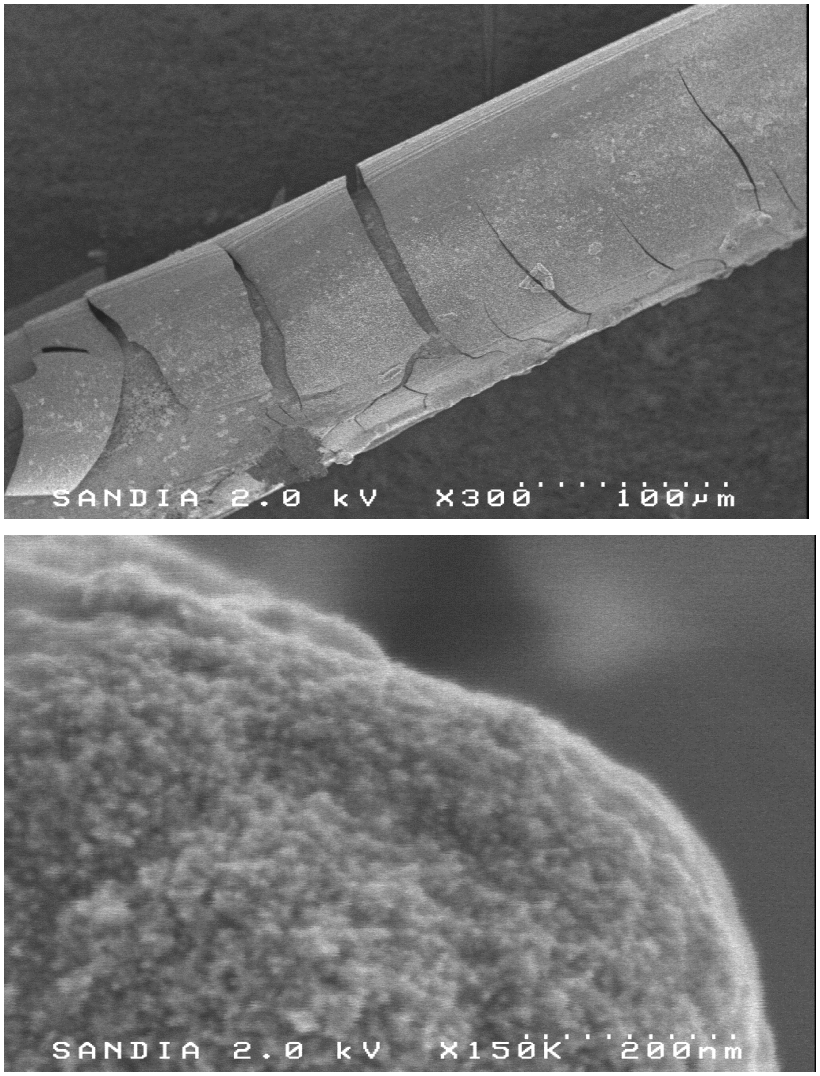


Cappillino et al., J Mater Chem A 1 602 (2013)

- Particles grow around well defined surfactant micelles by chemical reduction by H_2, yielding regular pores
- No control of particle size on longer length scales
- Particle size/shape is as important to storage material performance as pore size/shape

Chemical Reduction with Copper

- $Pd^{2+} + Cu^{0} \rightarrow Pd^{0} + Cu^{2+}$
- Pd takes shape of copper
- Surfactant can be added to reaction solution
- Surfactant yields good pore size on surface



Producing Uniform Copper Particles

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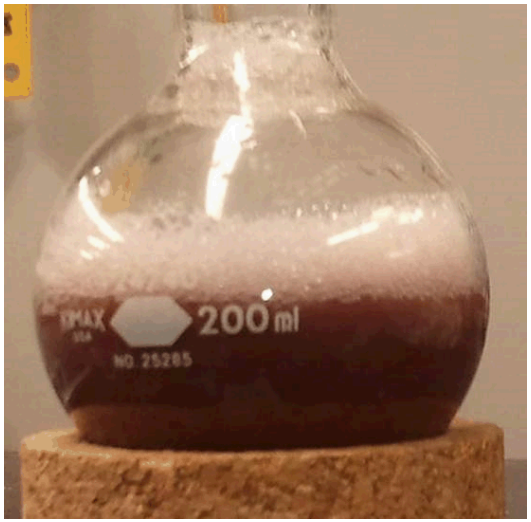
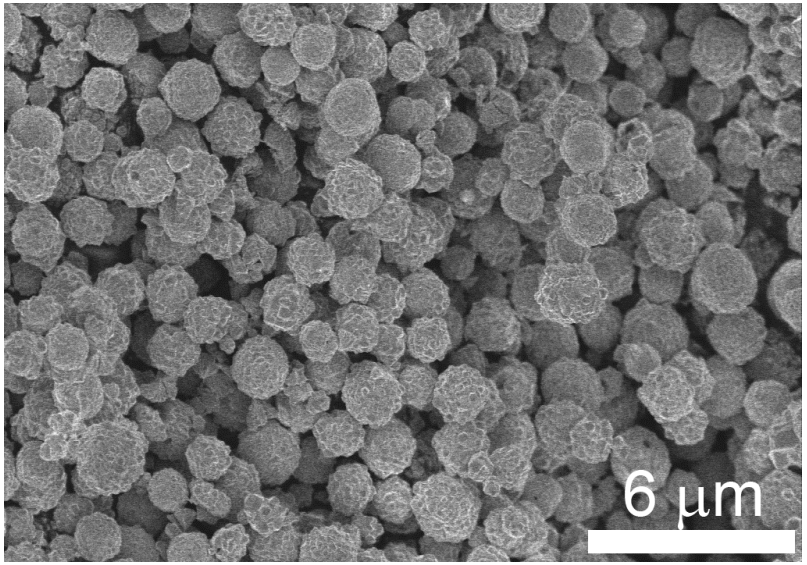
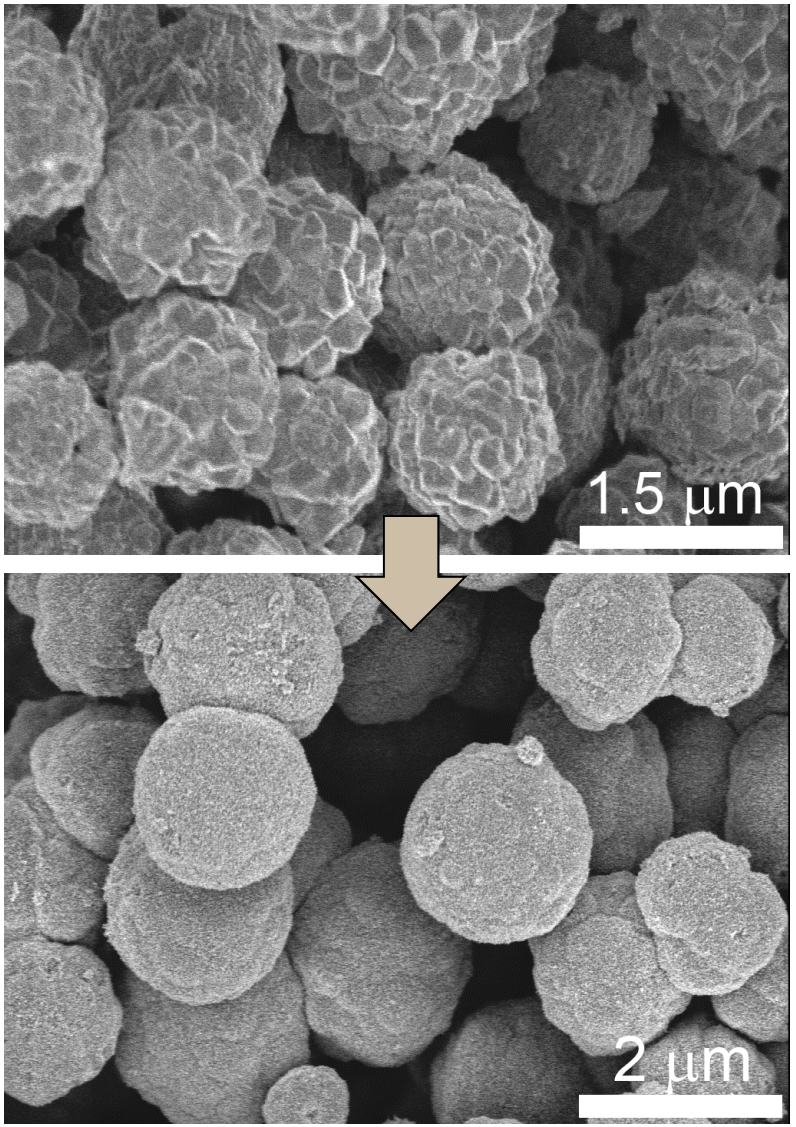
- Simple room temperature reaction
- Use variation of M. Bicer and I Sisman, Powder Tech 198 279 (2010)
- NaAscorbate + $CuSO_4$ → Cu
- Particles suspended in Pluronic F127 surfactant during synthesis to prevent aggregation
- Produces highly uniform spherical particles between 1 – 2 µm





Optimal conditions for Pd-Cu reduction

- 1:1 ratio Cu to Pd
- Cu dispersed in 1.0 wt% Pluronic F127 solution
- Presence of excess chloride required to slow reduction process and prevent uncontrolled growth
- Mixed at room temperature/ 2 - 3 days
- Geometrically self limiting reaction
- Easily scalable to batches >200 mg/ Possibly more



Uncontrolled Particle Growth

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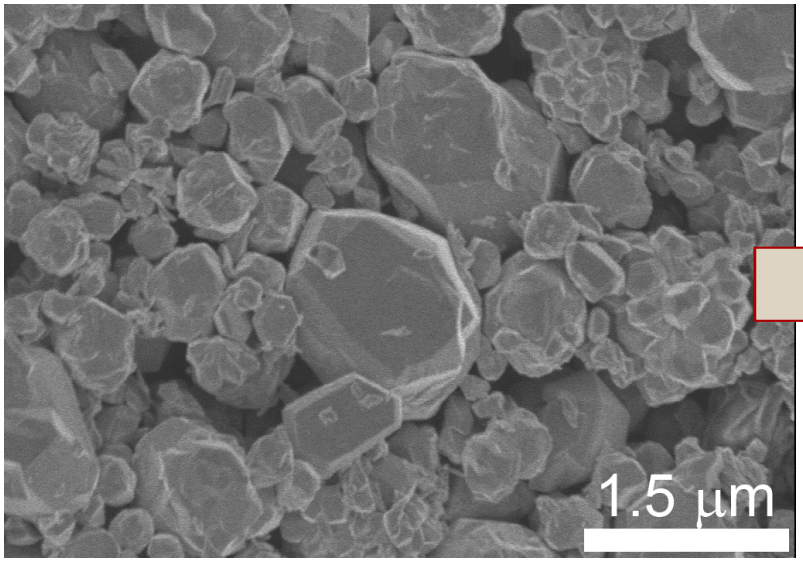
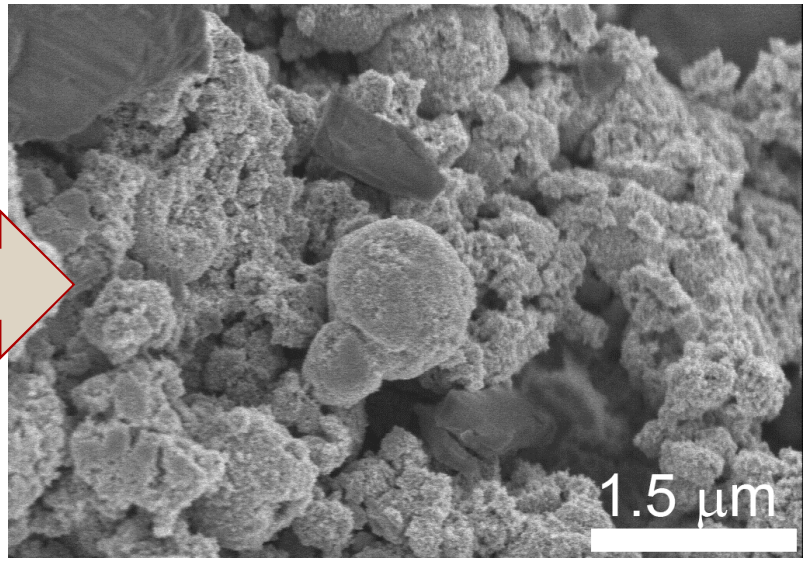
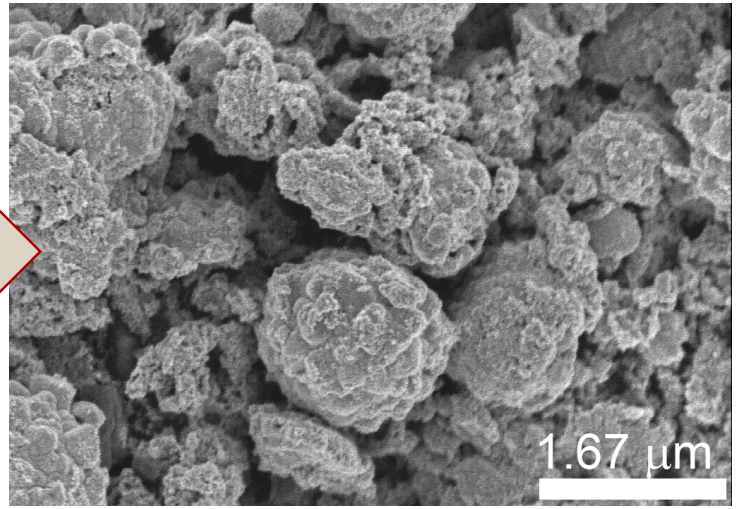
Non-Uniform Copper = Non-Uniform Palladium

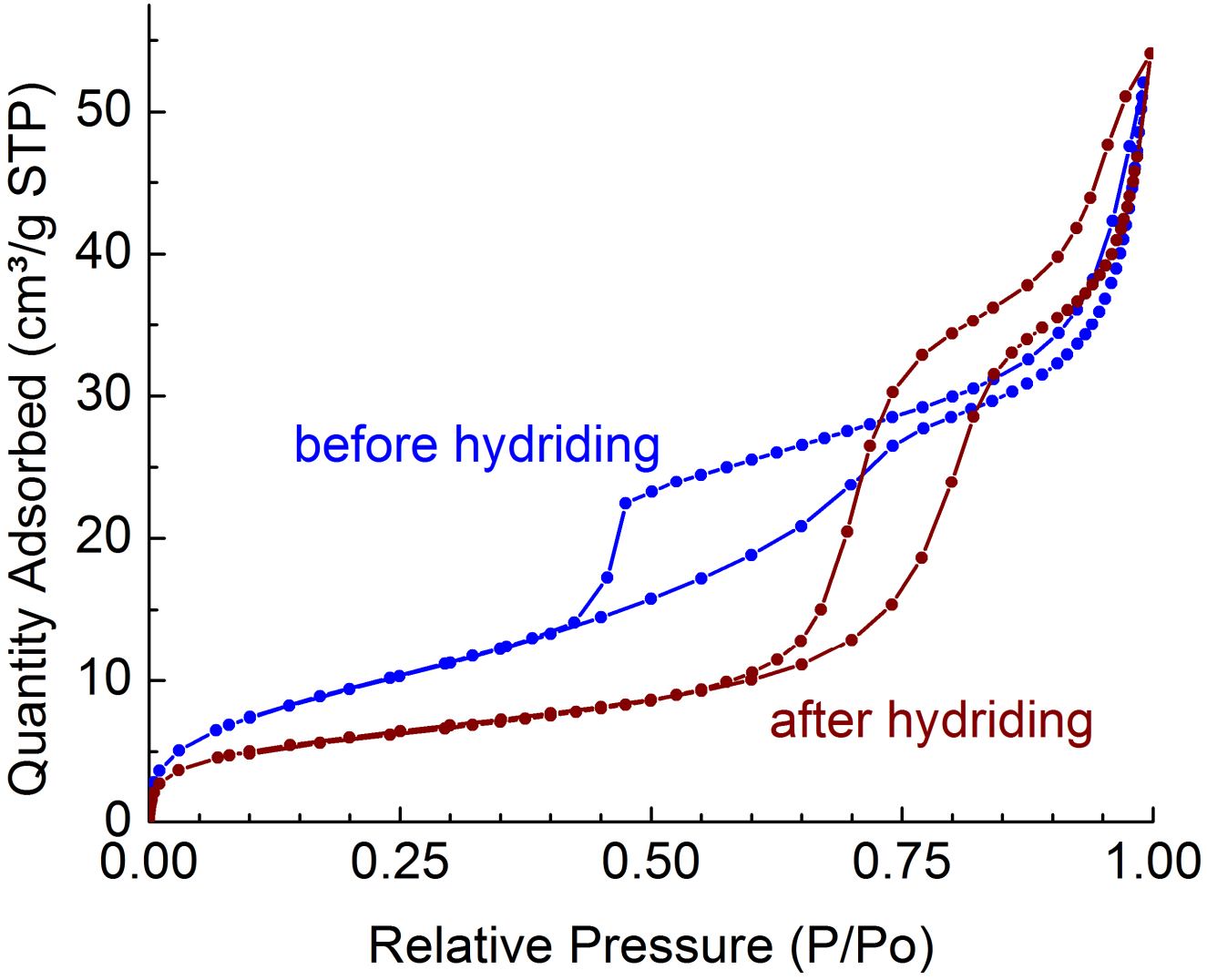




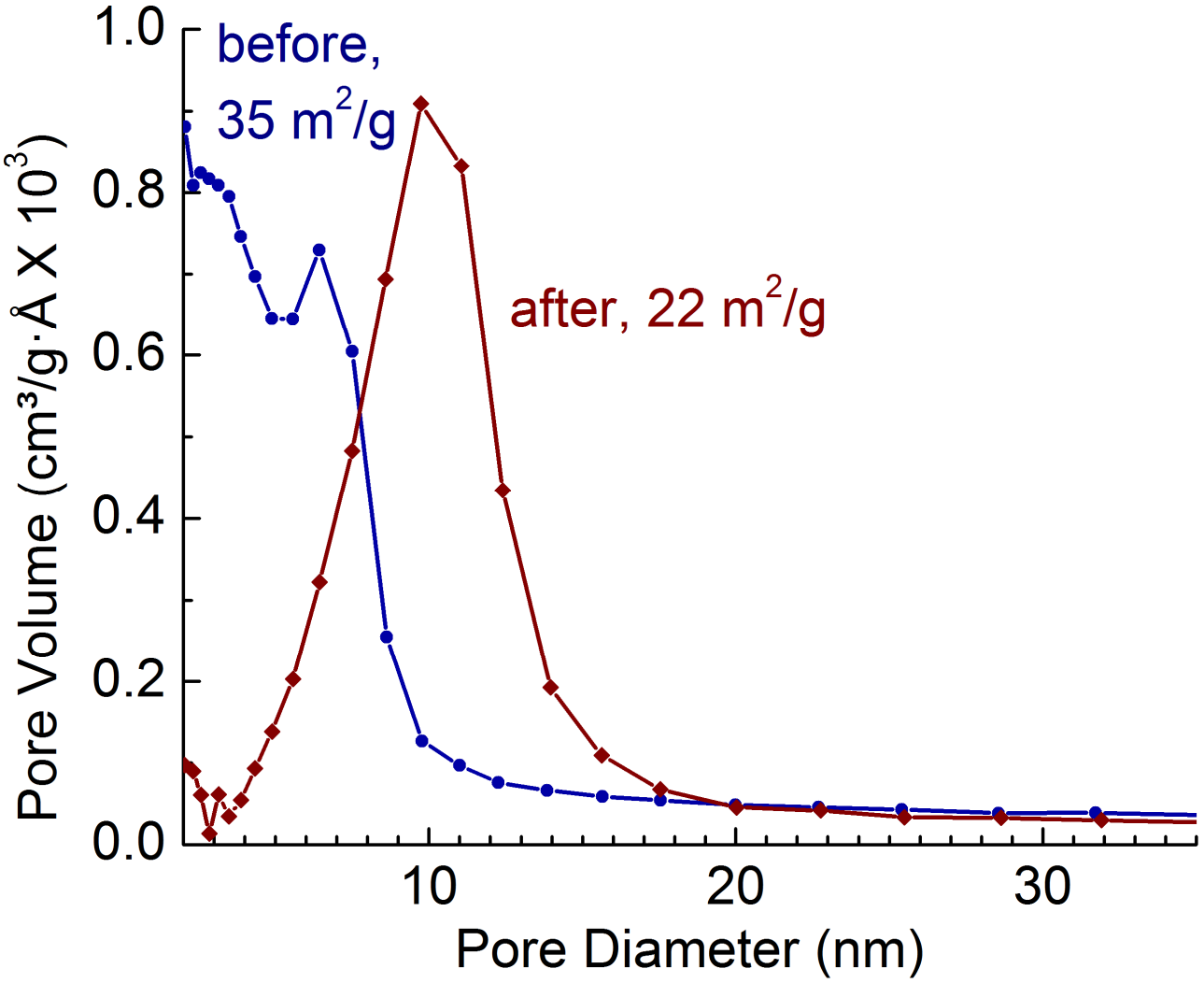
Reactions performed without the presence of excess chloride using particles with high uniformity produce similar results



Changes in Material During Hydriding

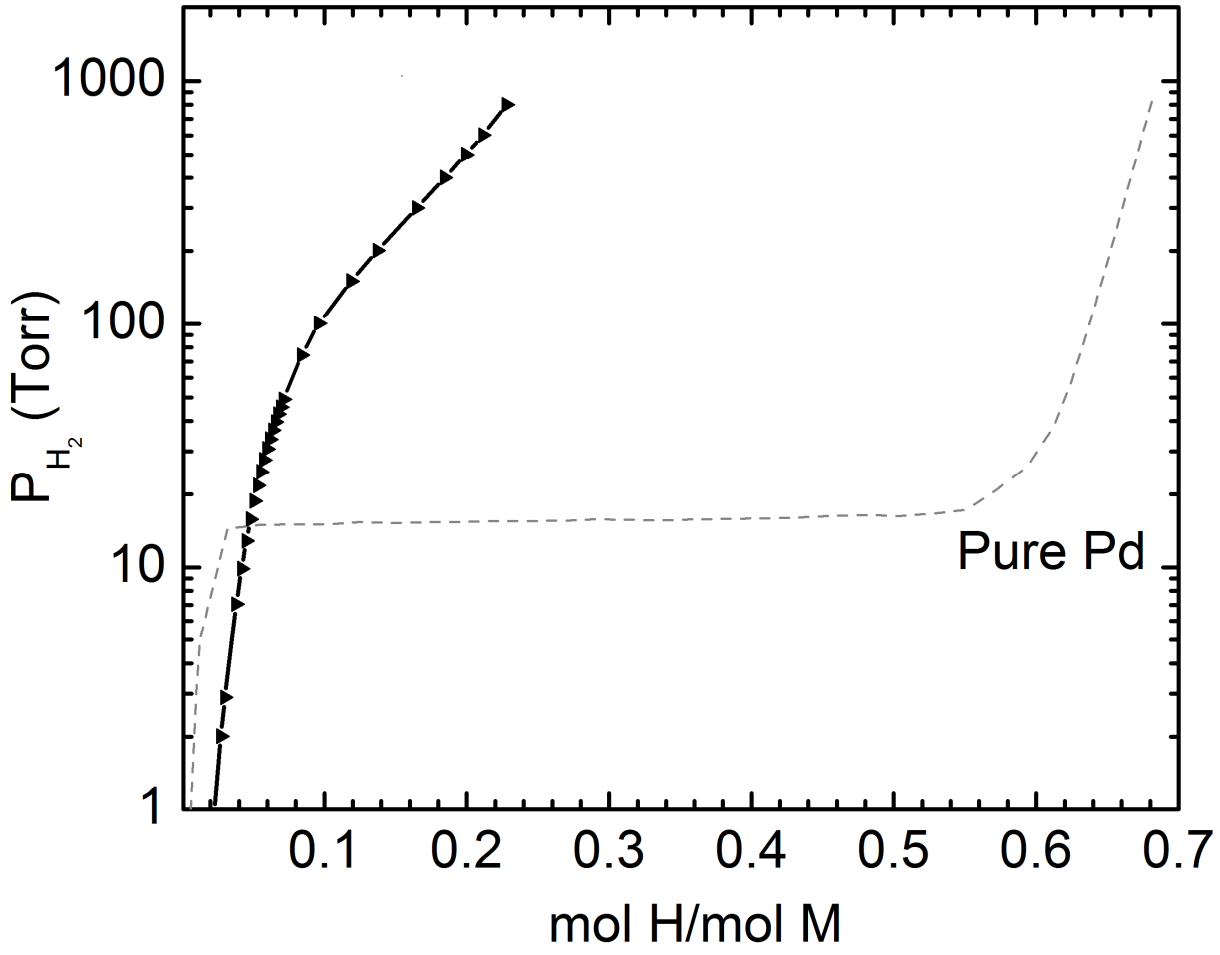


Pore Size Distribution Before and After Hydriding



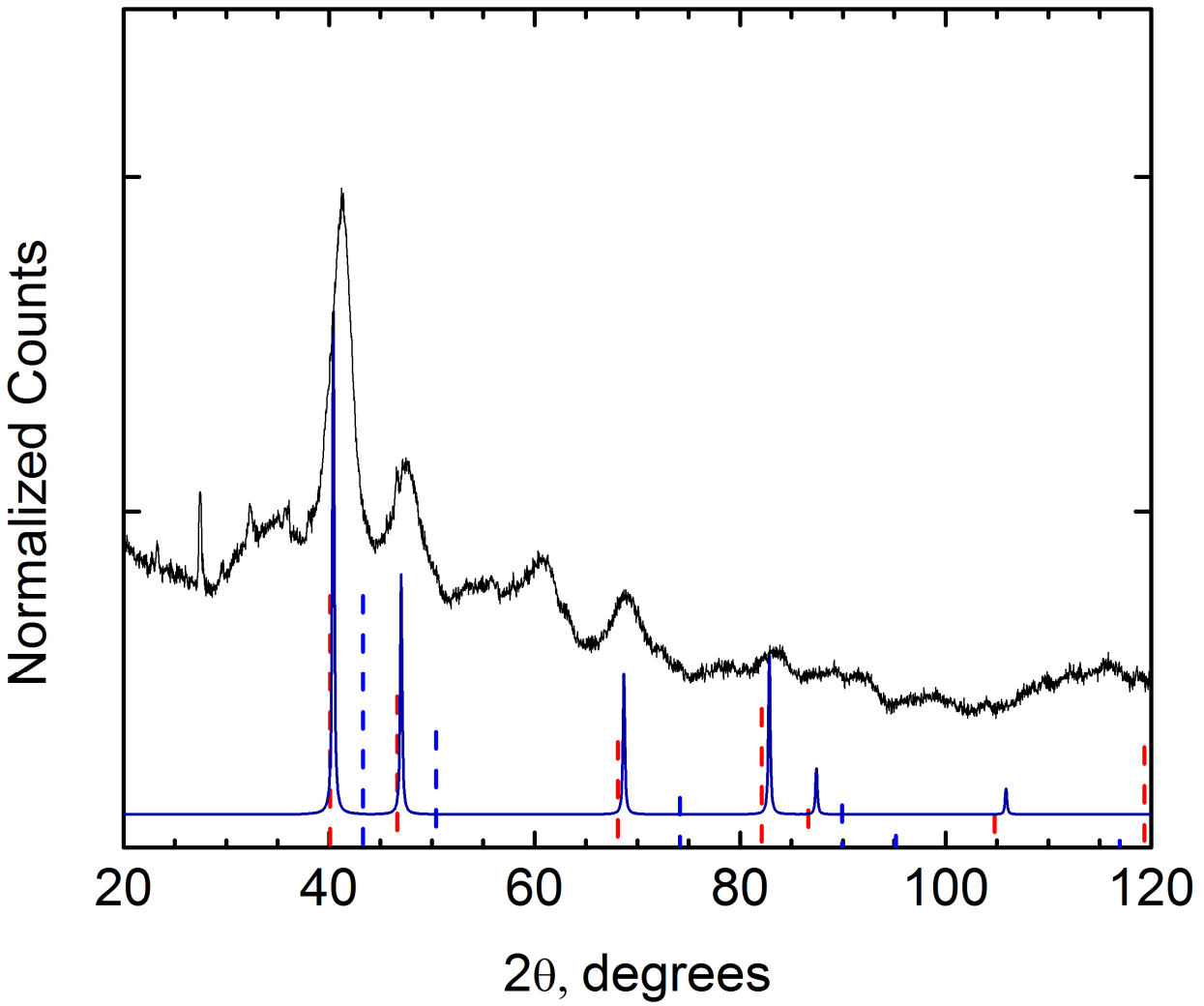
Measuring Absorption Capacity

- No visible plateau region
- Limited Absorption capacity in comparison to Pure Pd
- Further analysis of particles to determine composition



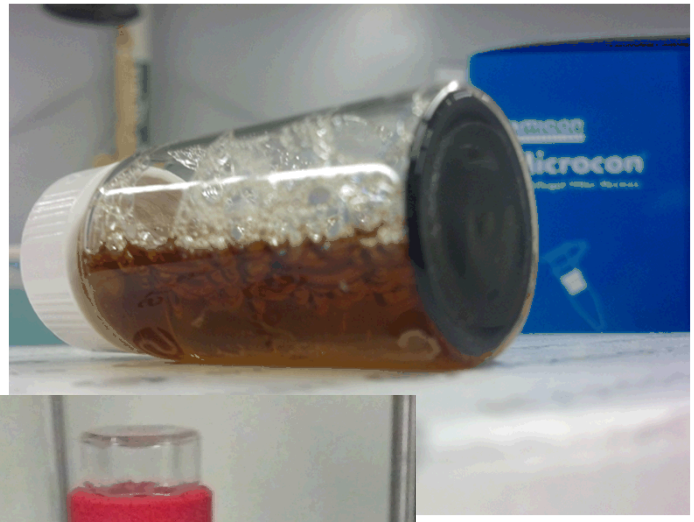
Materials Characterization and Analysis

- XRD anaylsis reveals presence of both copper and palladium
- Simulated reference peaks indicated particles are a Pd-Cu alloy rather than mix of both Pd and Cu particles
- Energy-dispersive X-ray spectroscopy (EDS) shows particles are composed of ~60% Pd/~40% Cu

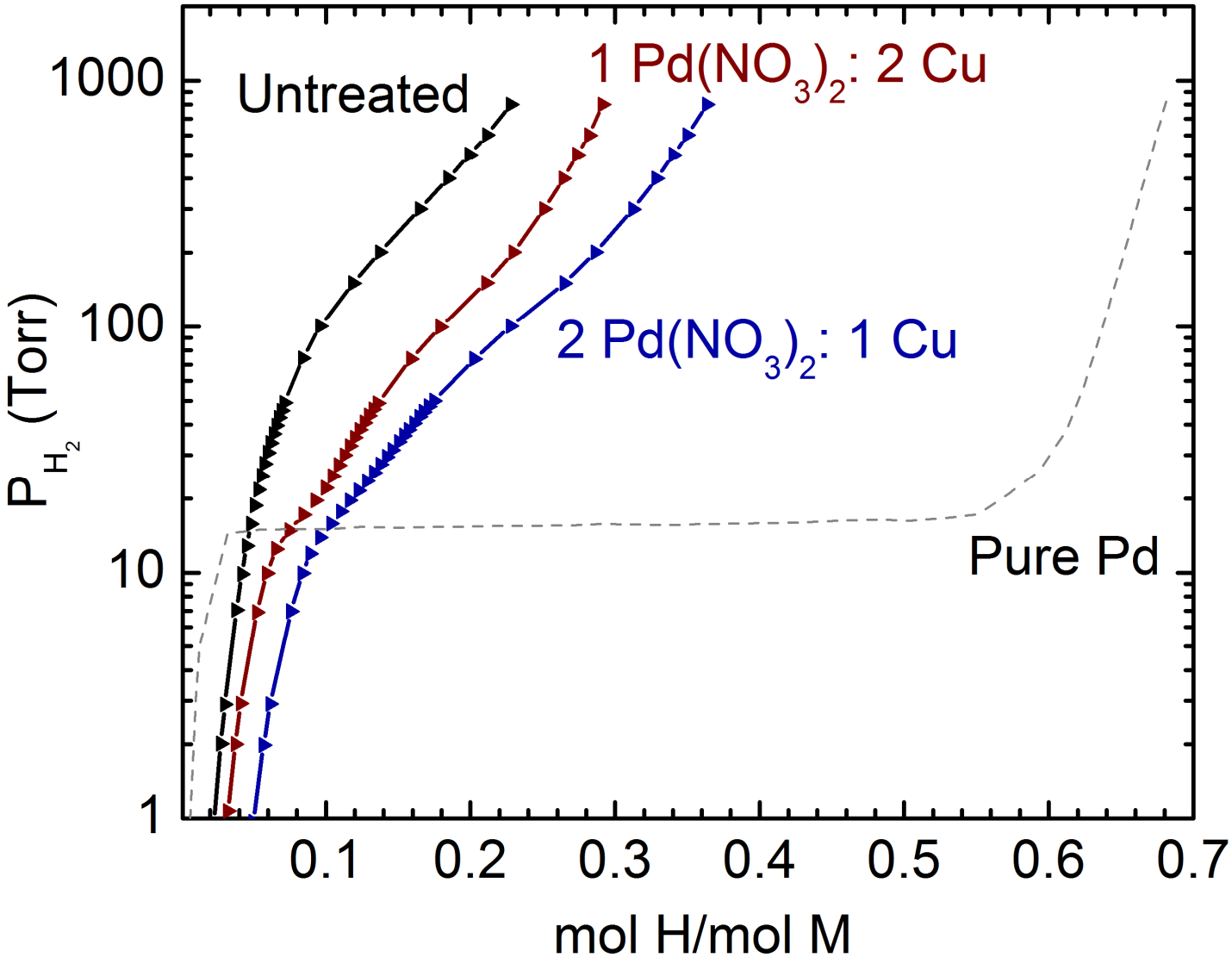


Chemical Etching to Remove Copper

- Use palladium nitrate to solution to chemically treat particles post synthesis
- $Pd(NO_3)_2$ has higher reduction potential than Pd ions in presence of excess chloride during synthesis
- More likely to react with residual Cu in product that is stabilized by alloying with Pd
- Two Treatments:
  1 $Pd(NO_3)_2$:2 Cu
  2 $Pd(NO_3)_2$:1 Cu



Improvements in Absorption Capacity



Conclusions

- Inexpensive procedure to produce highly uniform nanoporous Pd-Cu particles
- produce size- and shape-tunable particles based on the physical characteristics of the copper used as a reducing agent
- Results suggests possibility to scale to even greater quantities
- May be beneficial applications where achievement of maximum possible storage densities is not necessary eg. Hydrogen Gas/Isotope Separation
- Possibilities for biomedical and catalyst applications