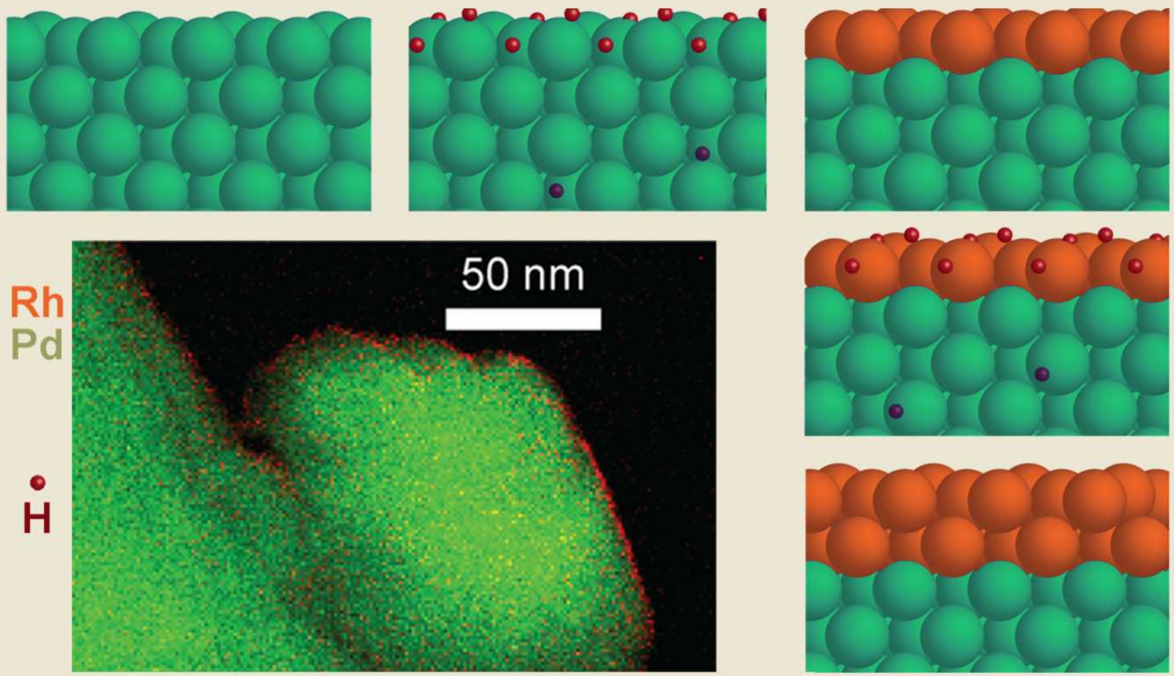
Synthesis of nanostructured, bimetallic, noble metal powders using Atomic Layer Electroless Deposition

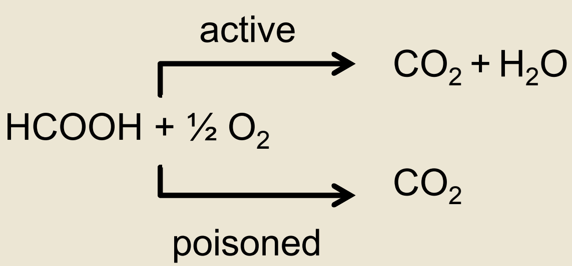
Patrick J. Cappillino, Joshua D. Sugar, Farid El Gabaly, Trevor Y. Cai, Zhi Liu, John L. Stickney and David B. Robinson



Division of Inorganic Chemistry
Chemistry of Materials
Tuesday, August 18, 2015

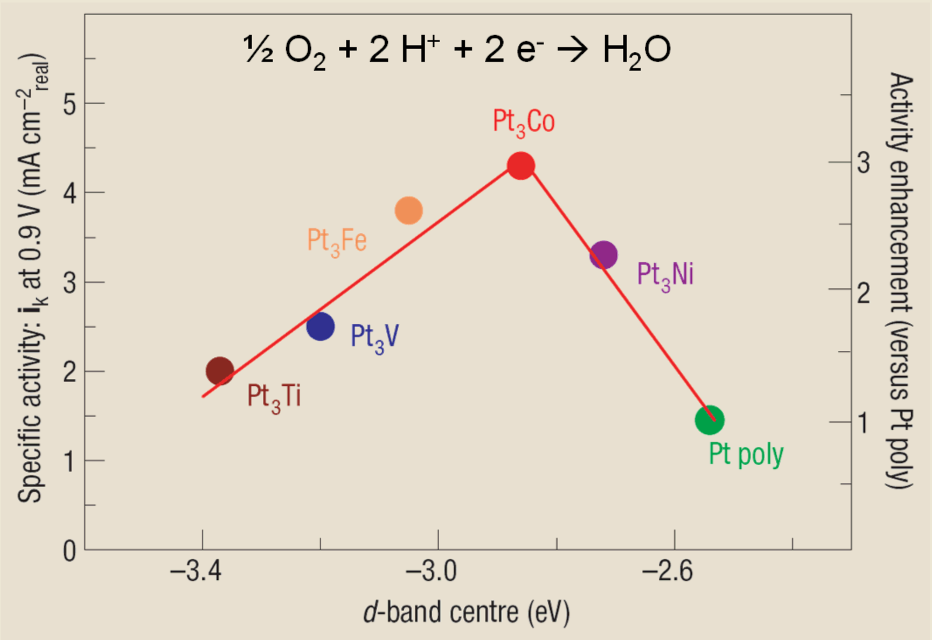
Adsorbed layers (adlayers) on catalysts enhance properties

Electro-oxidation of formic acid on Pt catalyst



- Adlayers such as Bi, Sb, As, Pd favor active pathway (reduce poisoning)

Oxygen reduction reaction on with bimetallic Pt catalysts



Hyunjoo Lee, *et. al.*, J. Am. Chem. Soc., 2008, 130, 5406-5407

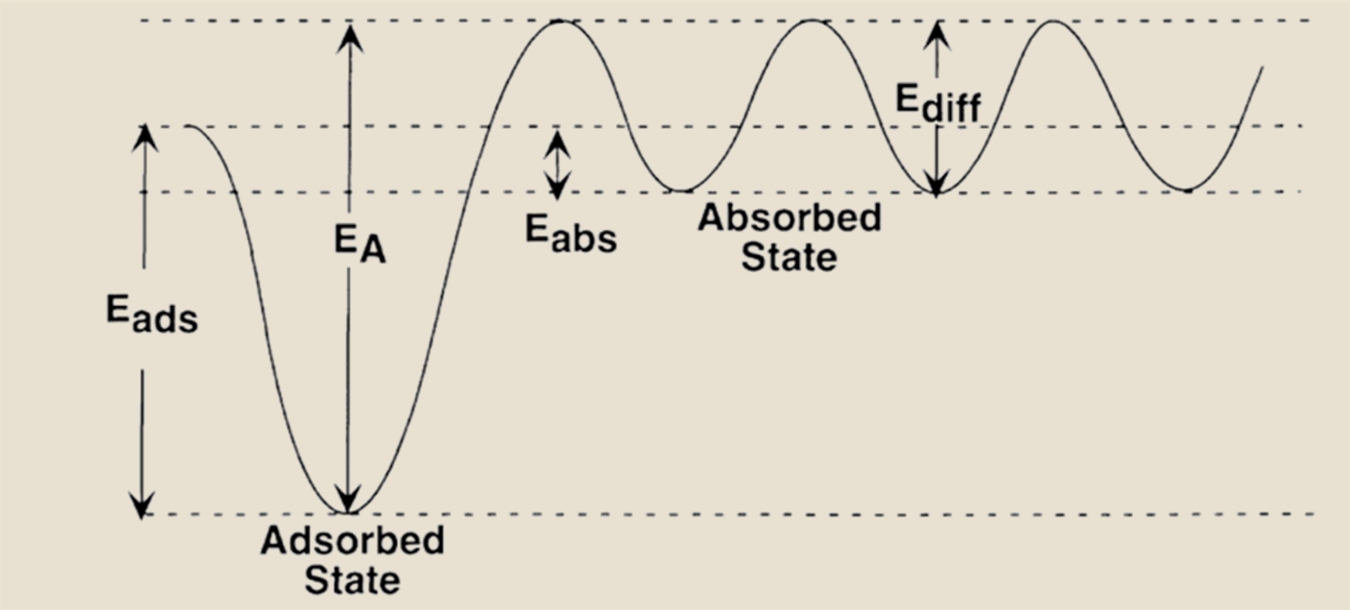
Stamenkovic, V. R., *et.al.*., Nature Materials, 2007, 6, 241-247

Surface modification should improve kinetics of hydriding and dehydriding Pd

$H_{2\,(g)} + Pd^0 \rightarrow PdH_x$ (X ~ 0.6)

- Surface Pd-H is very stable
- Large activation barrier for absorption
- Near-surface alloys destabilize surface hydrides, improve kinetics

Adsorbed hydride on Pd particle surface



Jeff Greeley and Manos Mavrikakis, J. Phys. Chem. B 2005, 109, 3460-3471

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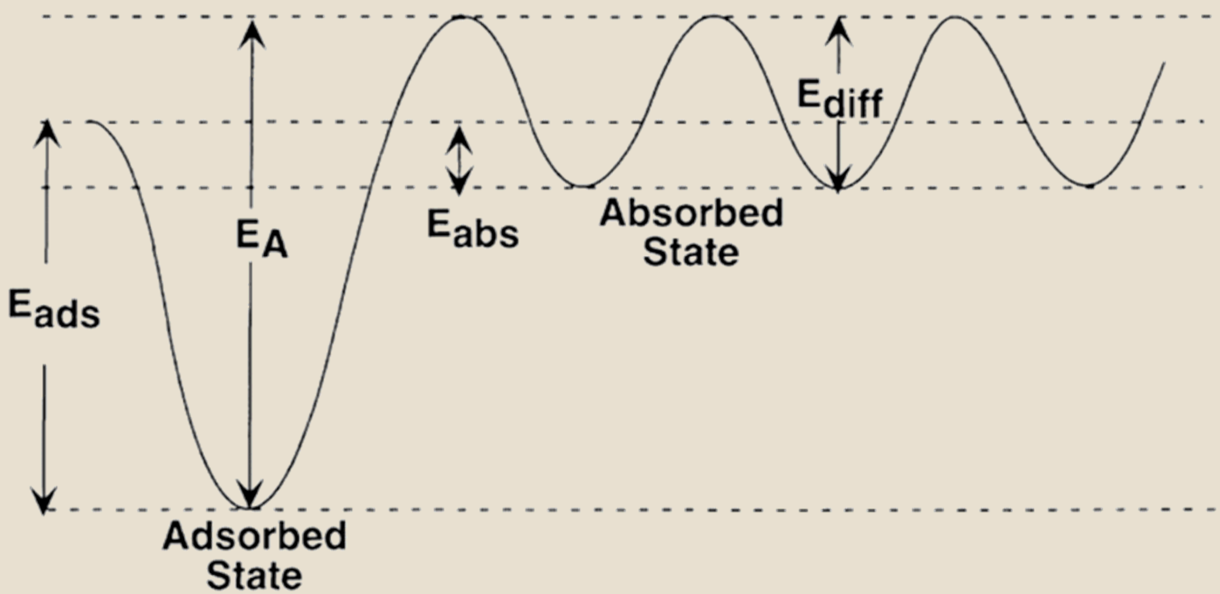
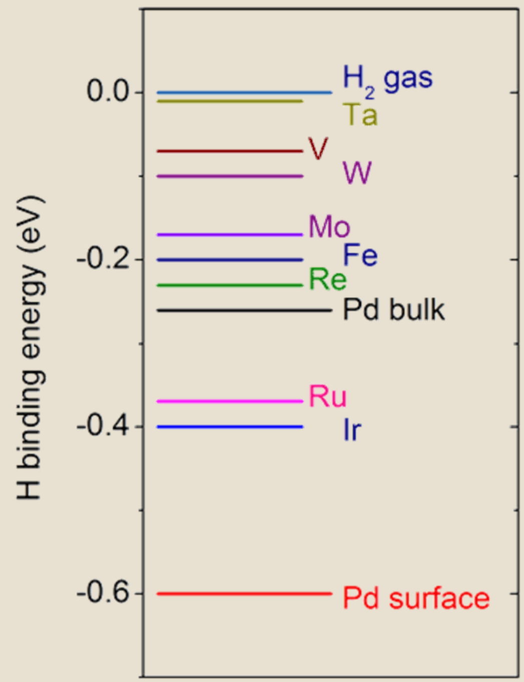
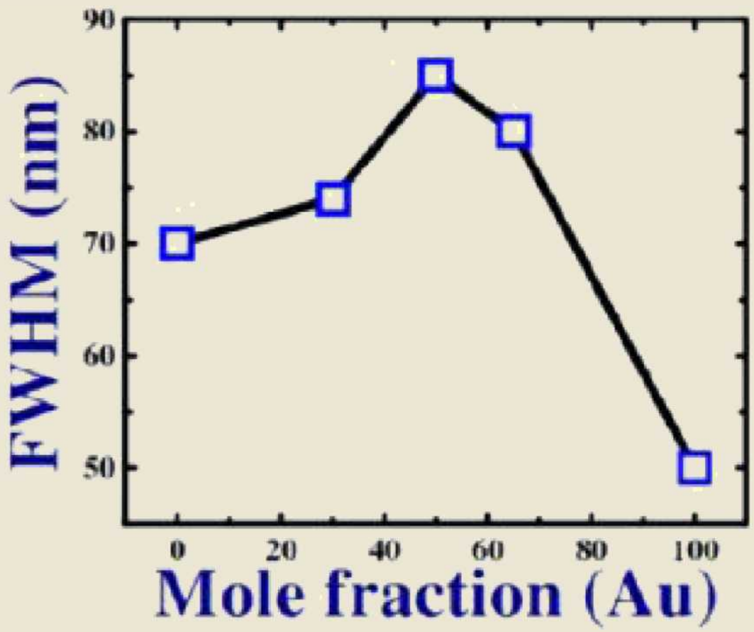


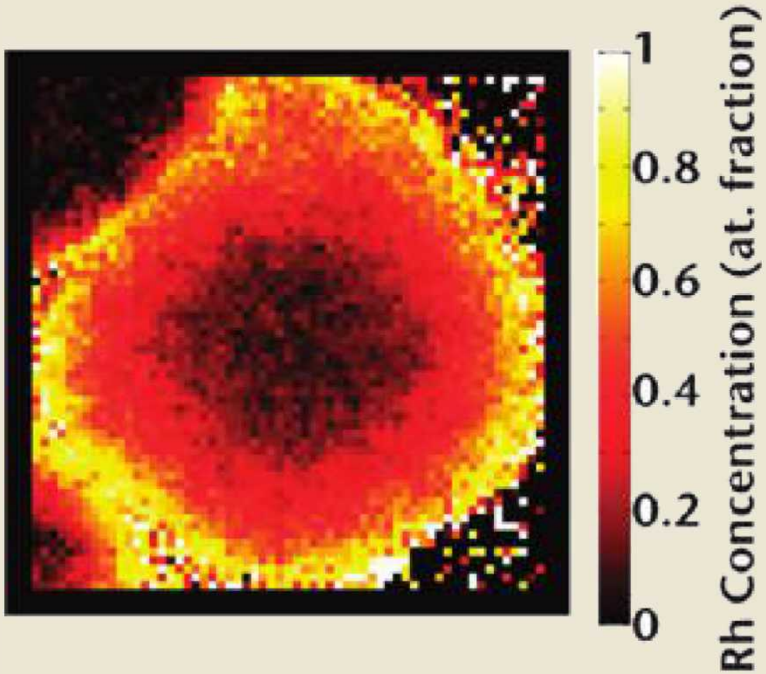


Jeff Greeley and Manos Mavrikakis, J. Phys. Chem. B 2005, 109, 3460-3471

Co-reduction, physical methods → Poor control



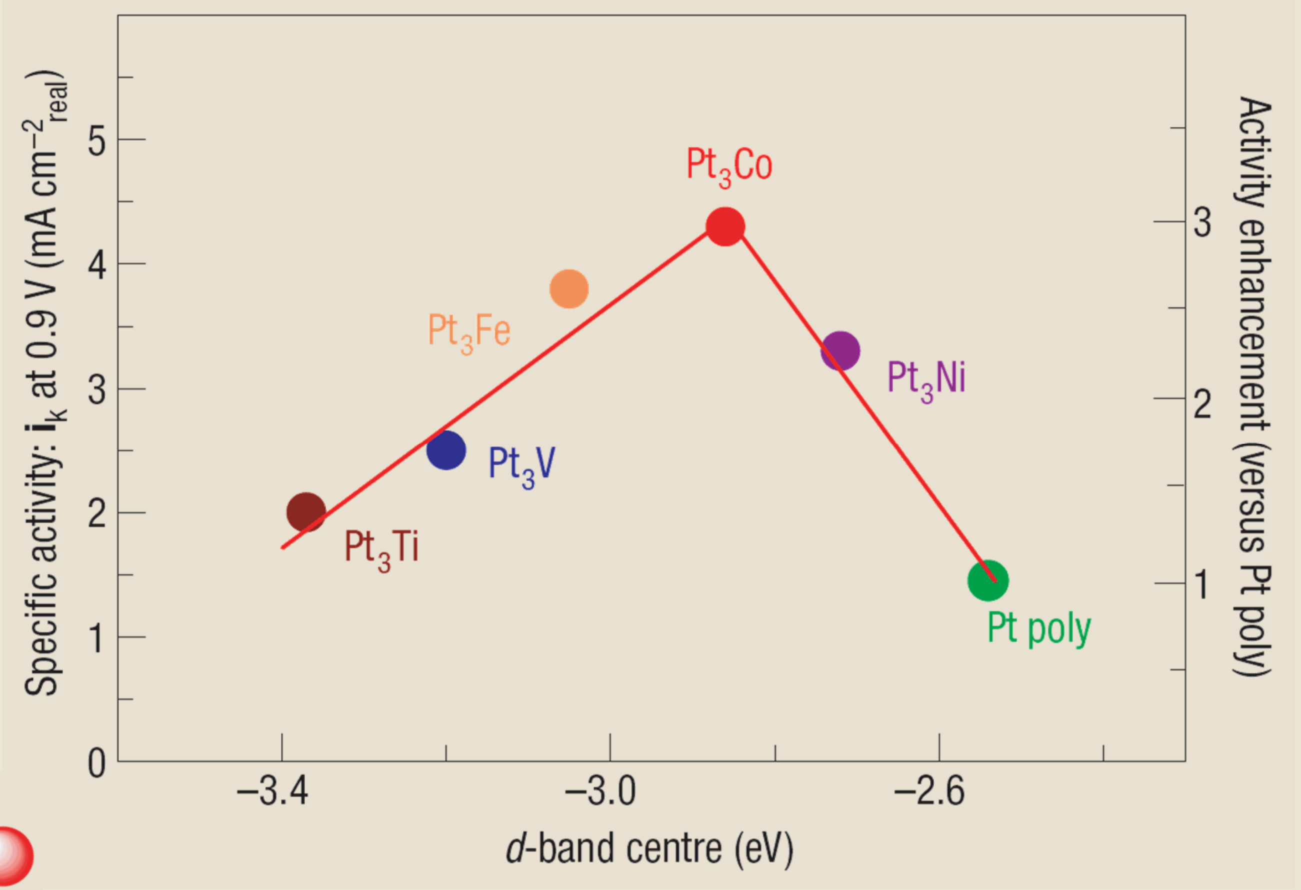
Different size, different composition from laser ablation



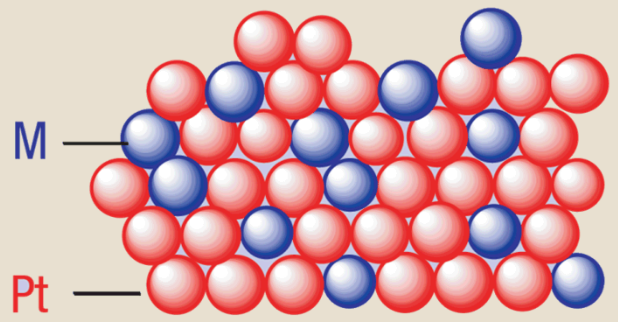
Differing kinetics of reduction lead to heterogenous composition

Podagatlapalli, G. K. *et al.*, *J. Phys. Chem. C* **2015**, *119* p.16972 Ong, M. D, *et al.*, *Chem Mater* **2012,** *24* (6), p. 996

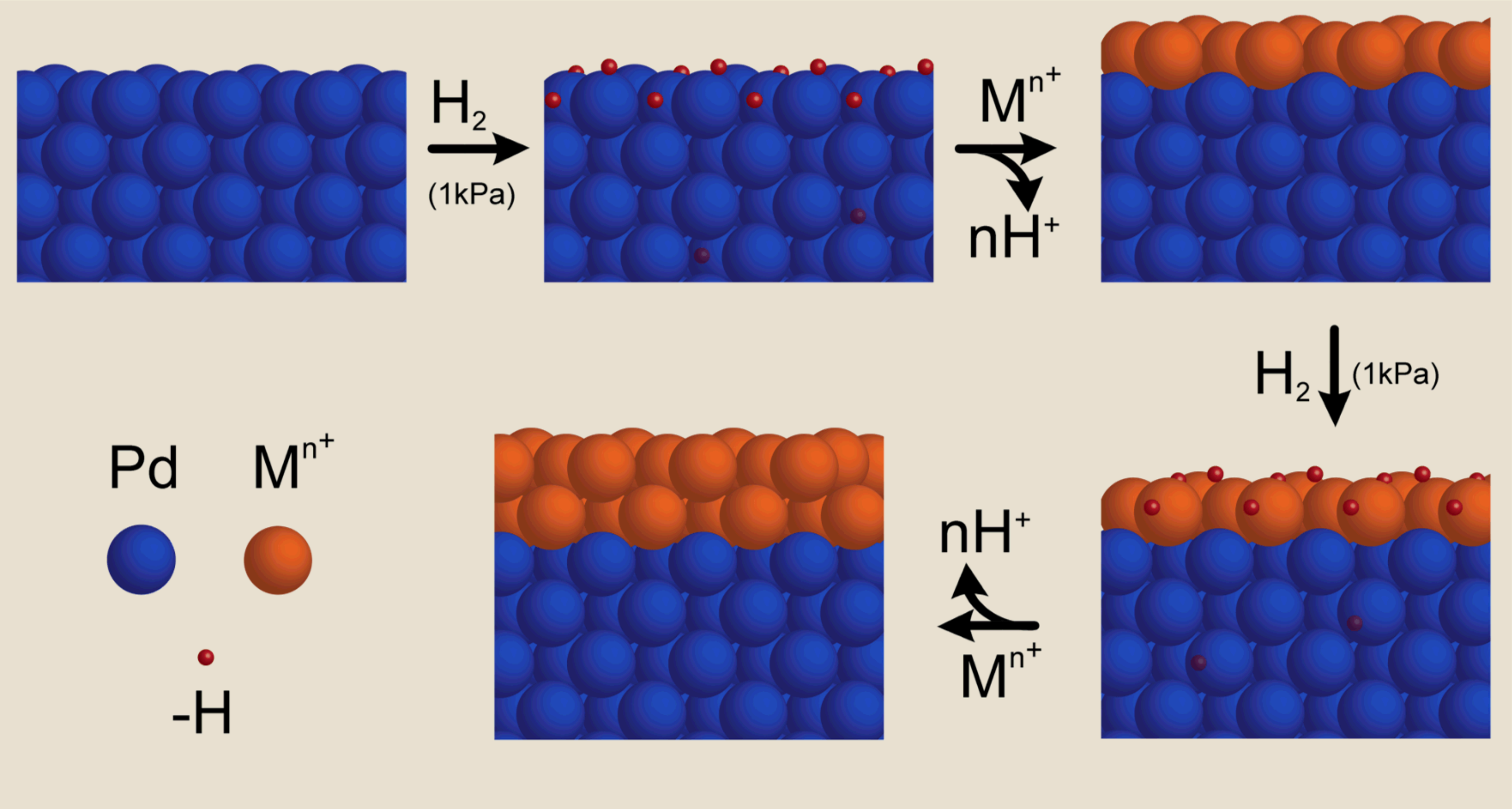
Co-reduction, physical methods → Poor control



Sputtered surface:



Atomic Layer Electroless Deposition (ALED)

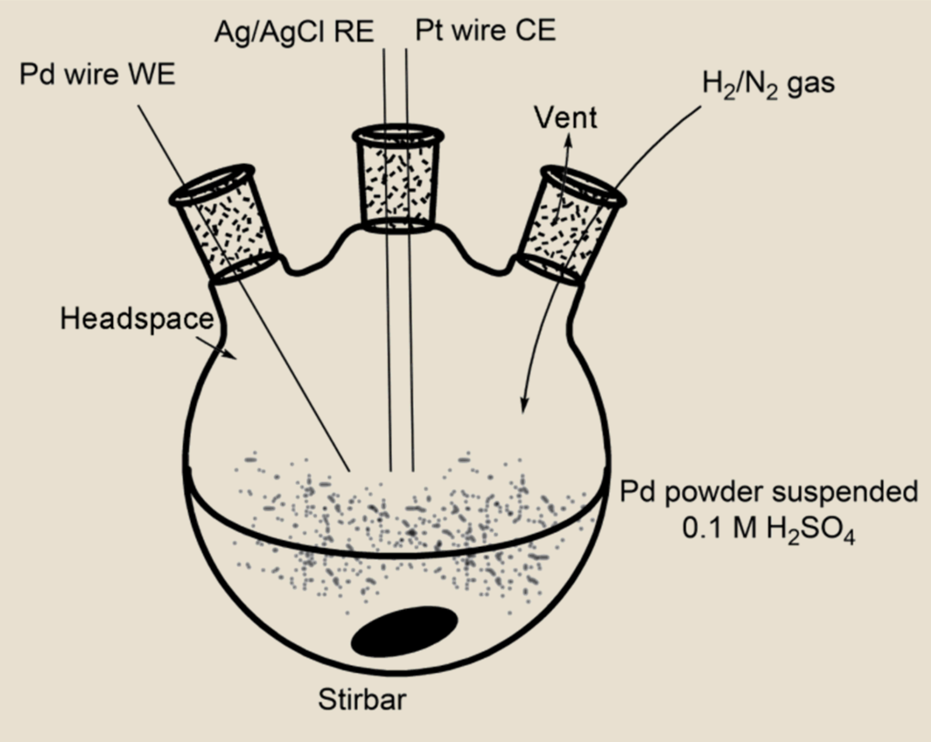


room temperature, “wireless”, amenable to “rough” surfaces with high surface area

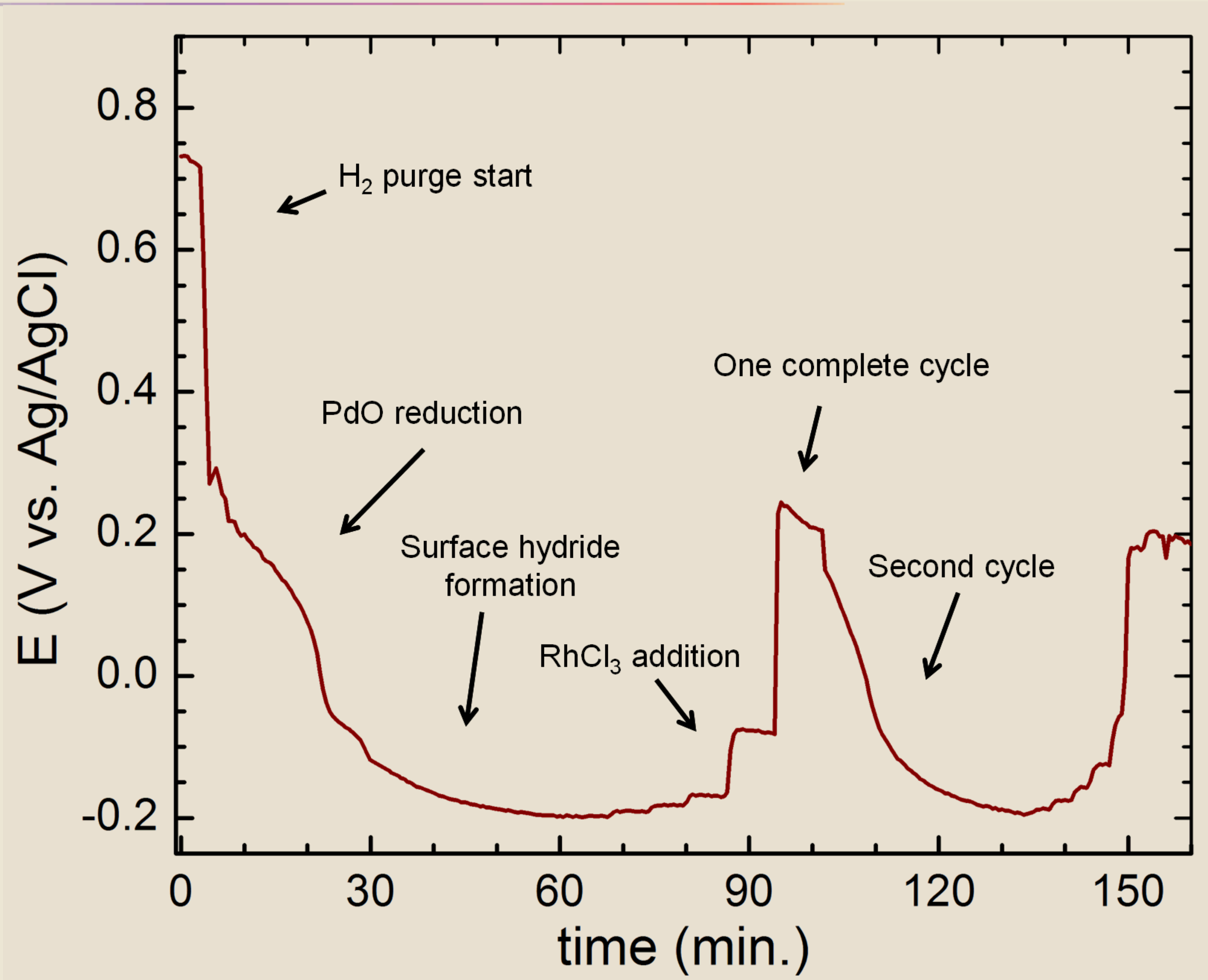
Cappillino, P. J., *et al.*, *Langmuir* **2014,** *30* (16), 4820-4829.

Simple Apparatus for EL-ALD

- Pd powder suspended in electrolyte
- Reagent gas (1% H_2/N_2)/inert gas source
- Metal salt added by syringe
- Electrodes to measure progress of reaction

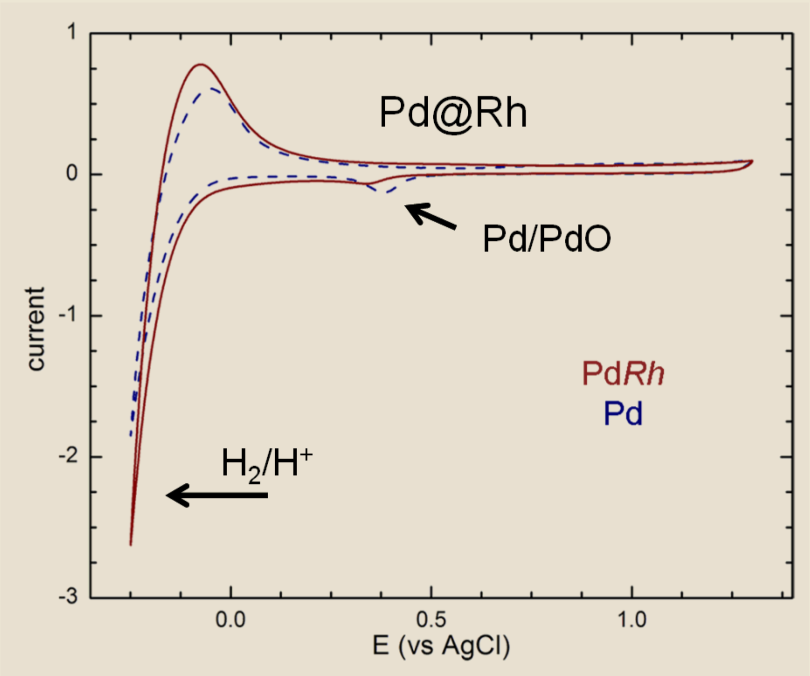


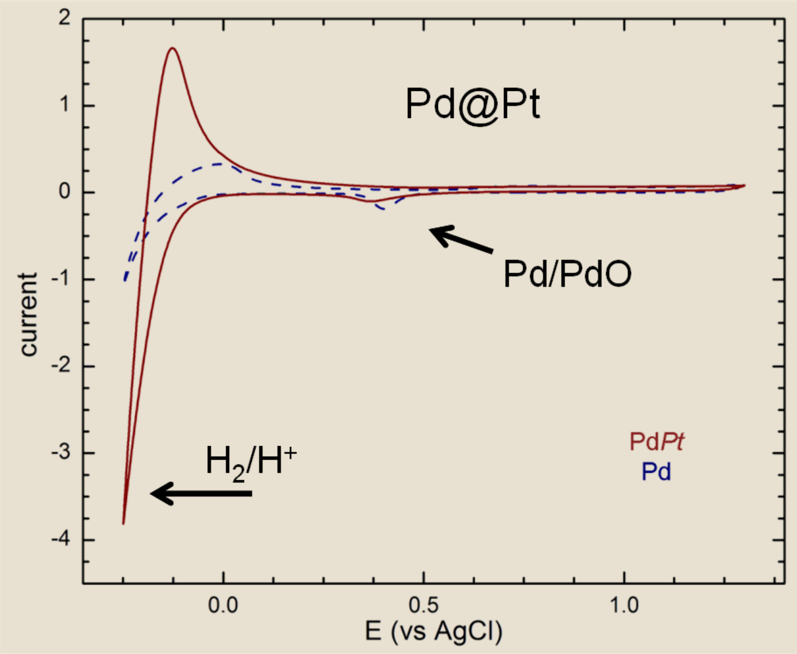
Monitor open circuit potential to follow reaction



Cappillino, P. J., *et al.*, *Langmuir* **2014,** *30* (16), 4820-4829.

Cyclic voltammetry of Pd test wire before and after deposition of adlayer of Rh (left) and Pt (right)





- Adlayer blocks Pd/PdO
- improved hydride/dehydride kinetics

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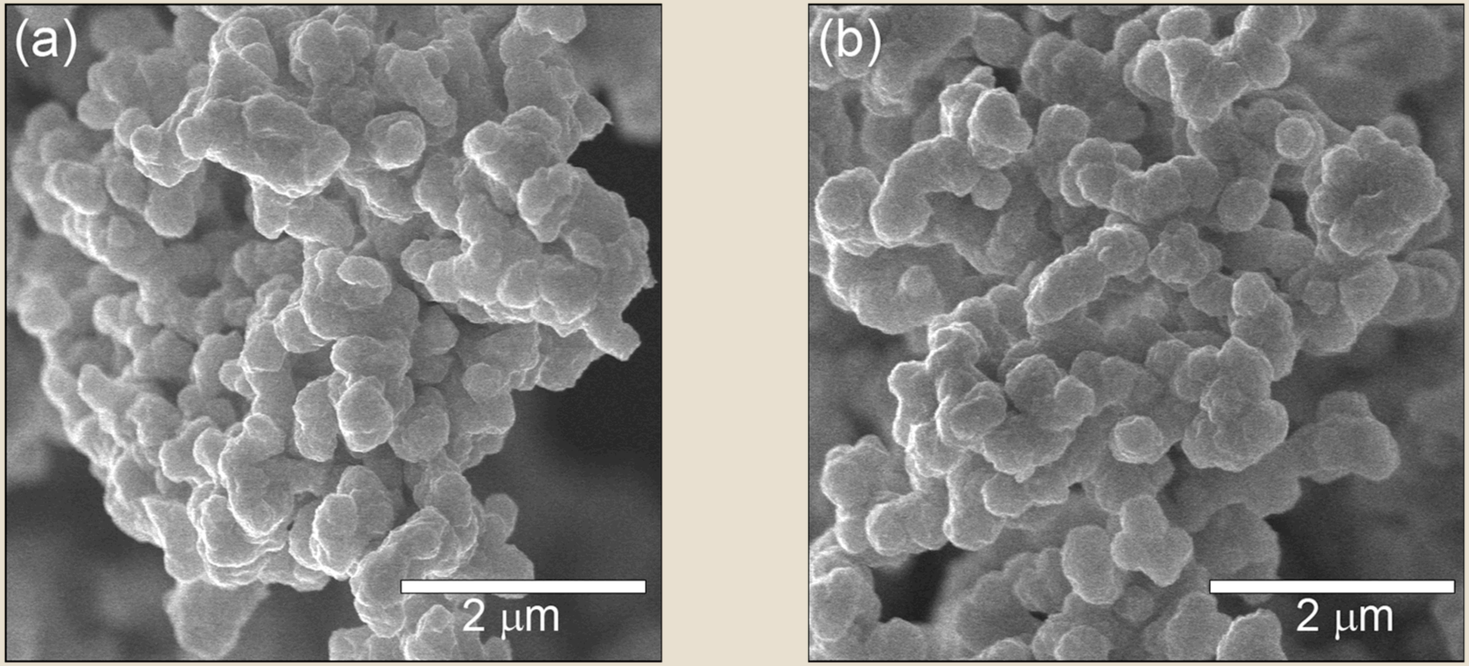
No change to particle morphology after two cycles of ALED of Rh on Pd



(a) Pd powder before deposition (b) Pd powder after 2 cycles of ALED

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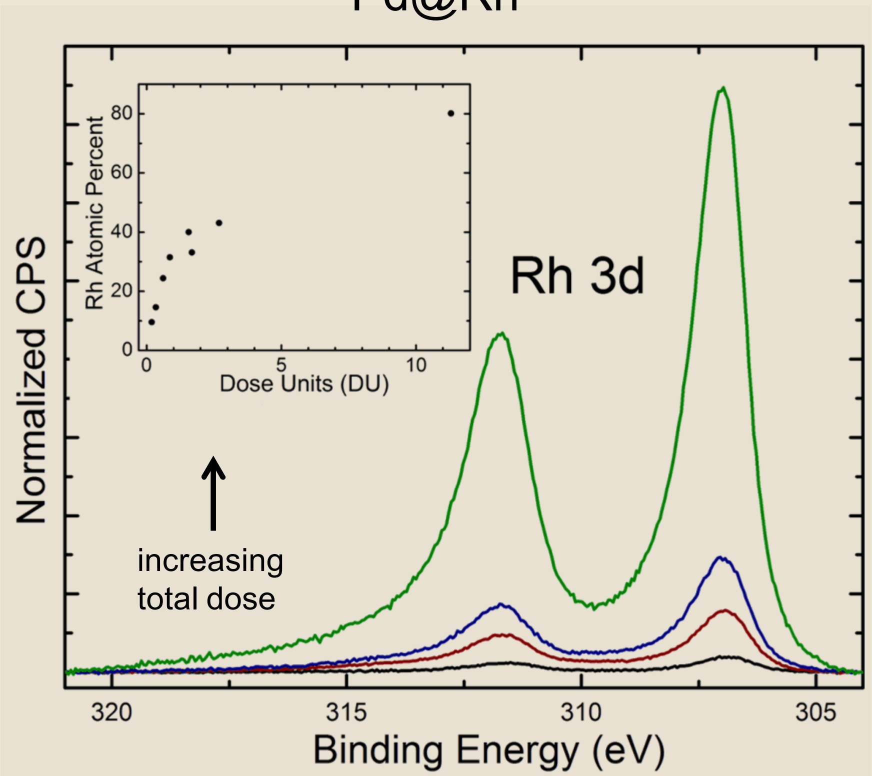
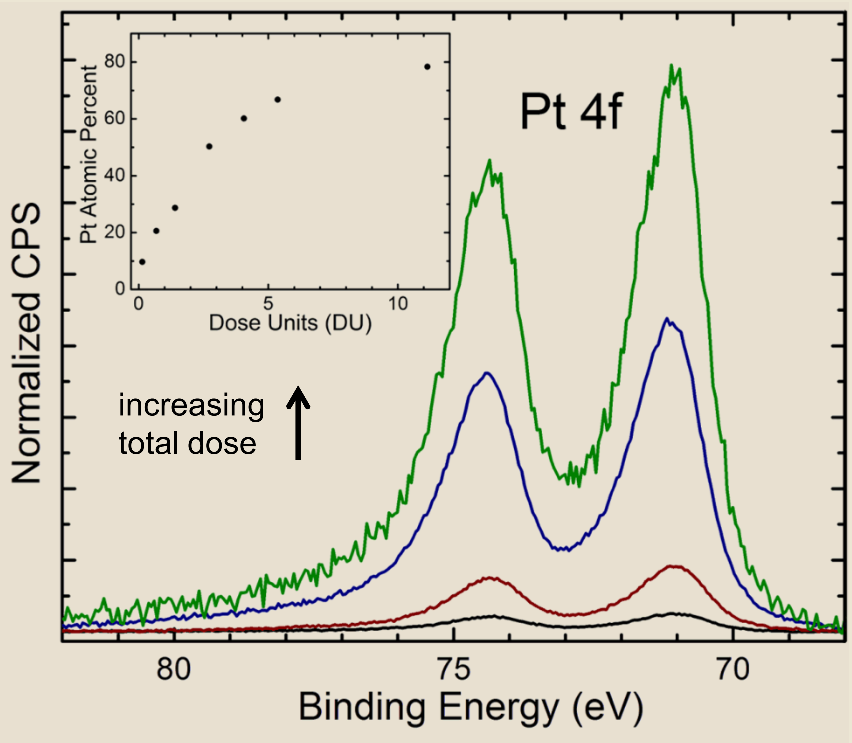
More cycles, more metal deposited (by X-ray Photoelectron Spectroscopy)

Pd@Rh



Pd@Pt



Rh and Pt peaks normalized to Pd peak at 335 eV

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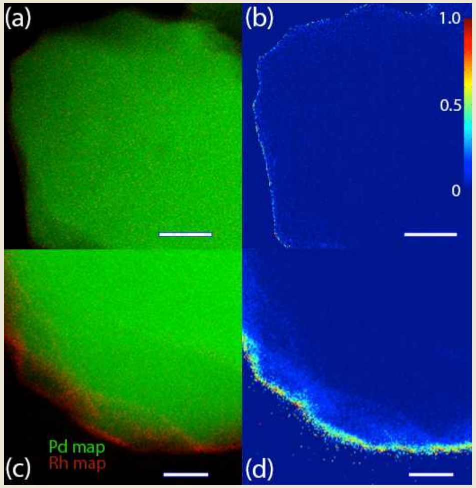
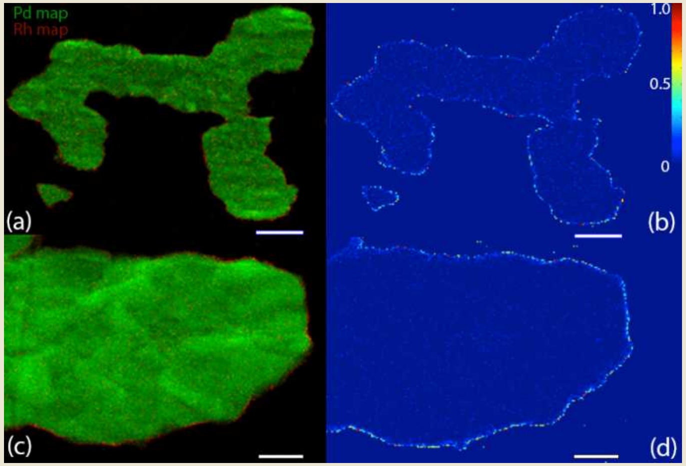
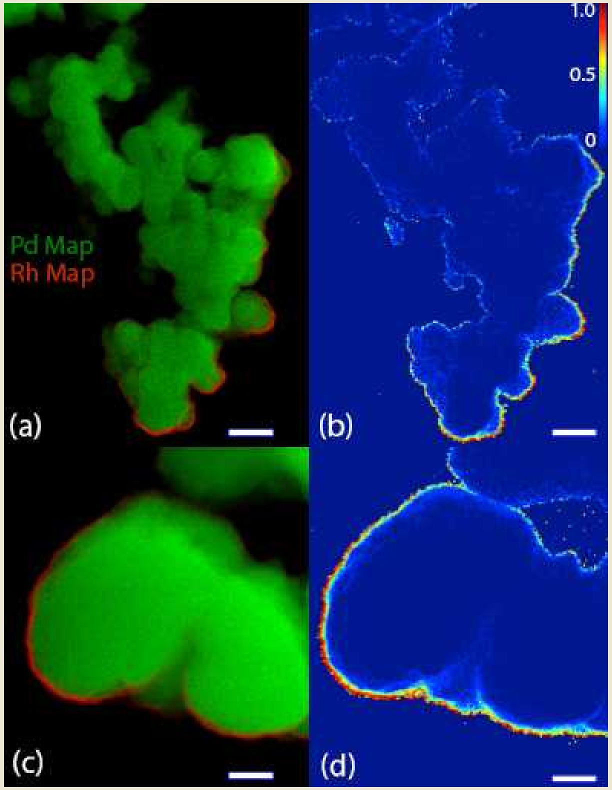
STEM-EDS confirms thickness control for Pd*Rh*





One cycle, **3.9** nm avg
scalebar = 500 nm (a,b)
scalebar = 150 nm (c,d))

Two cycles, **5.5** nm avg
scalebar = 250 nm (a,b)
scalebar = 60 nm (c,d))

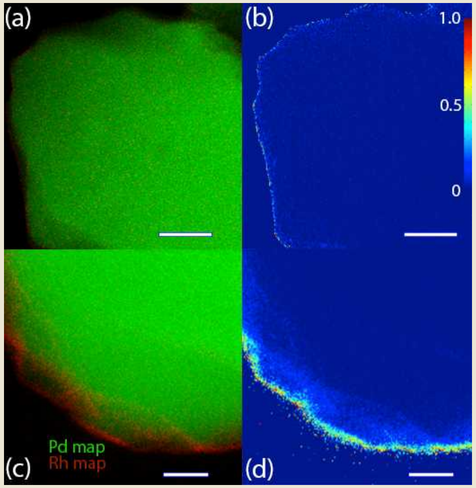


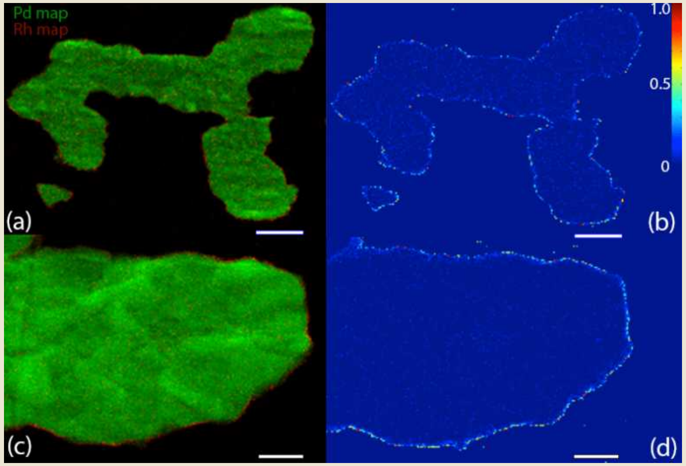
Eight cycles, **21.7** nm avg
scalebar = 500 nm (a,b)
scalebar = 20 nm (c,d))

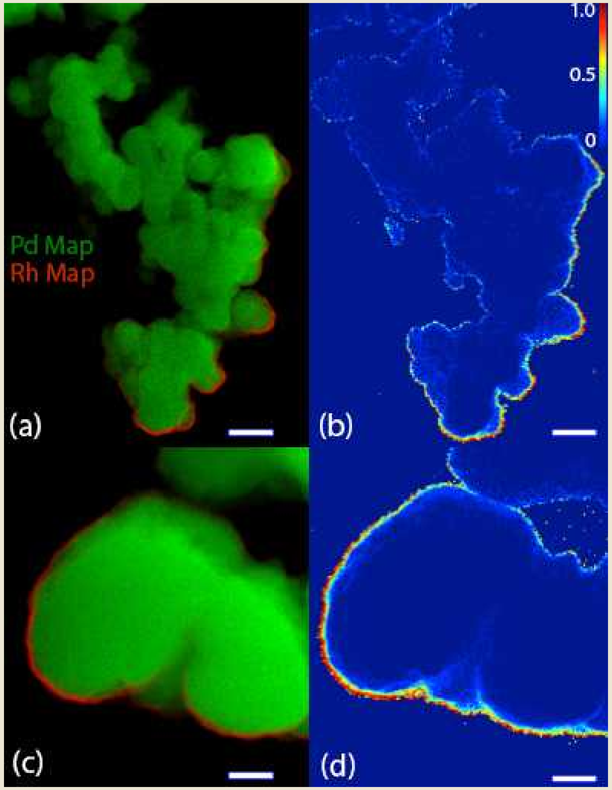
- *Increasing Rh thickness on Pd*Rh *with more cycles of deposition*

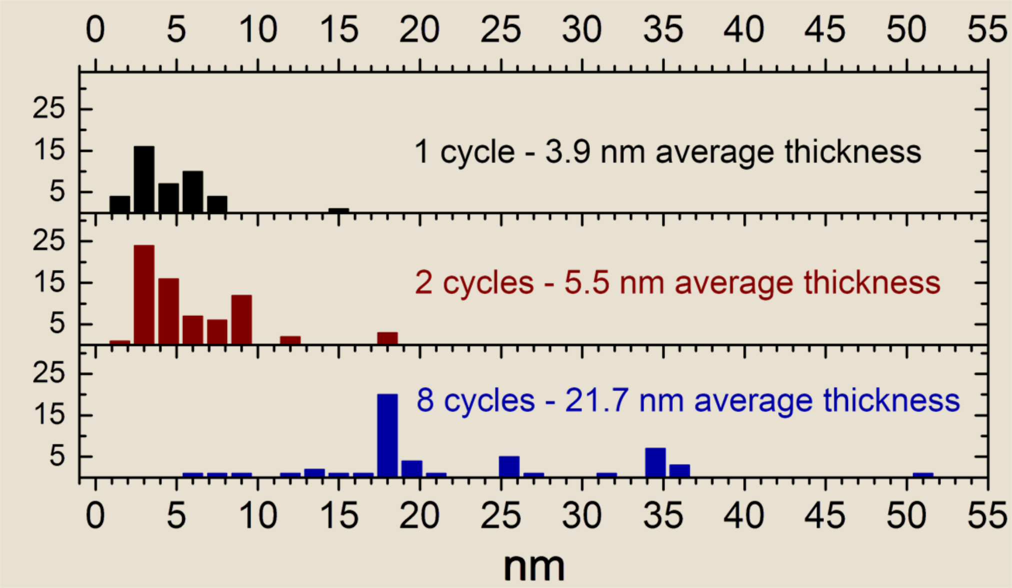
TEM images by Joshua D. Sugar at Sandia National Lab, Livermore, CA, unpublished

STEM-EDS confirms thickness control for Pd*Rh*



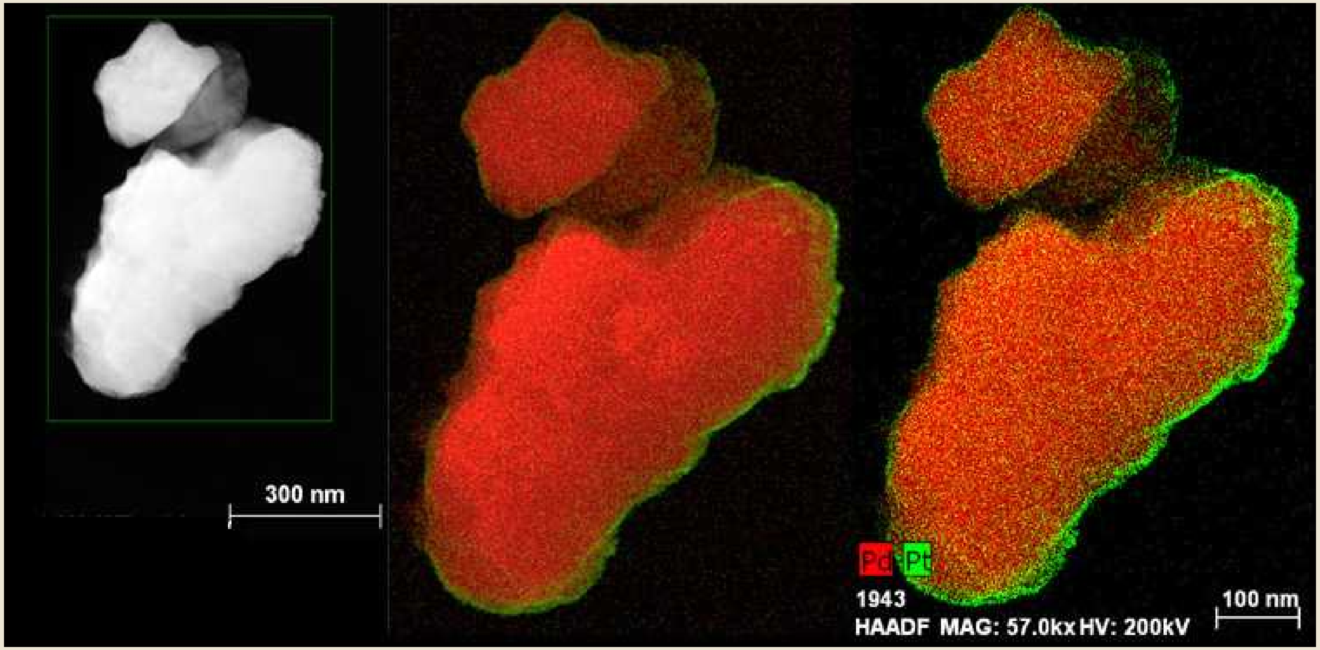


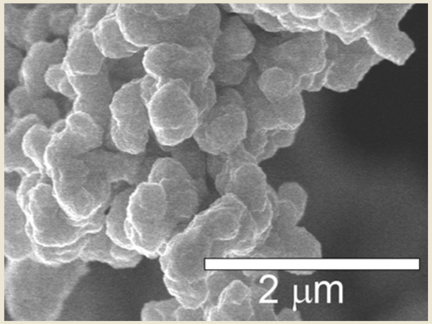




TEM images by Joshua D. Sugar at Sandia National Lab, Livermore, CA, unpublished

After initial concern, Pd*Pt* looks good



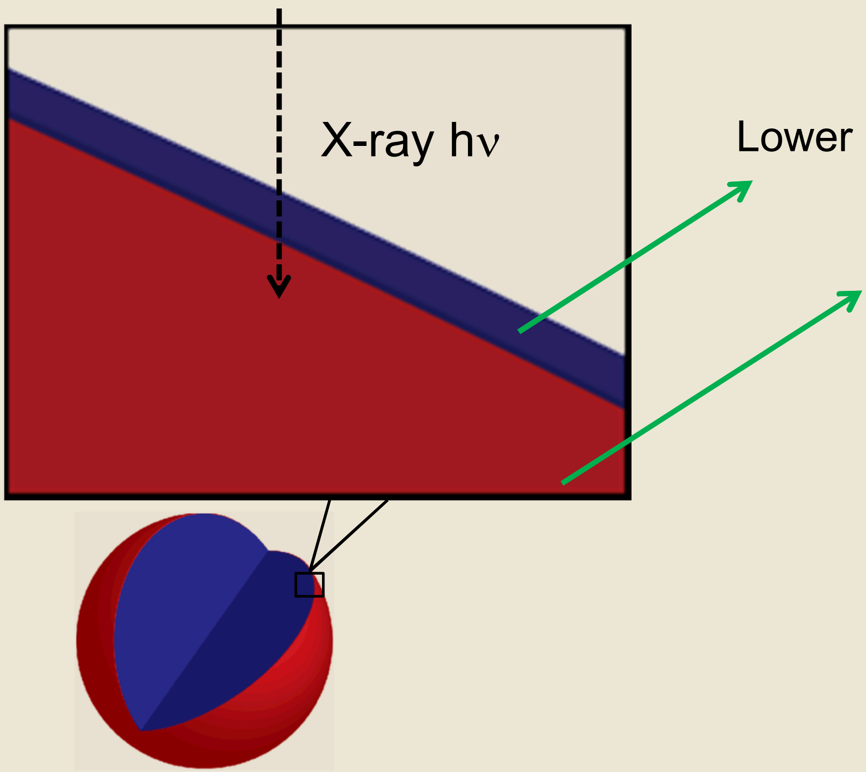


← *Keep in mind: aggregation*

TEM images by Joshua D. Sugar at Sandia National Lab, Livermore, CA, unpublished

Energy Resolved Depth Profile (XPS)

At synchrotron, incident photon energy ($h\nu$) can be tuned, $KE = h\nu - BE$

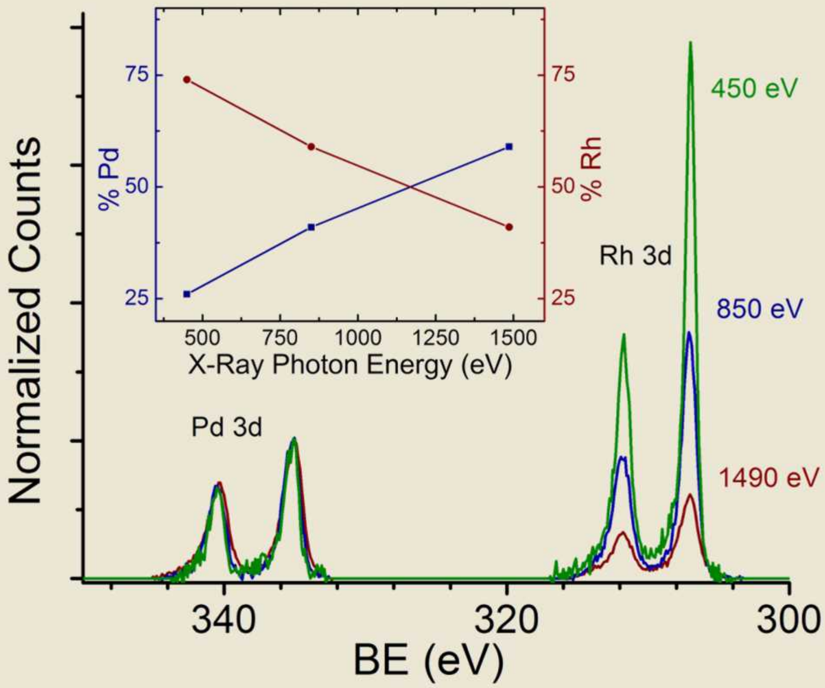


Lower energy photoelectrons are more surface sensitive

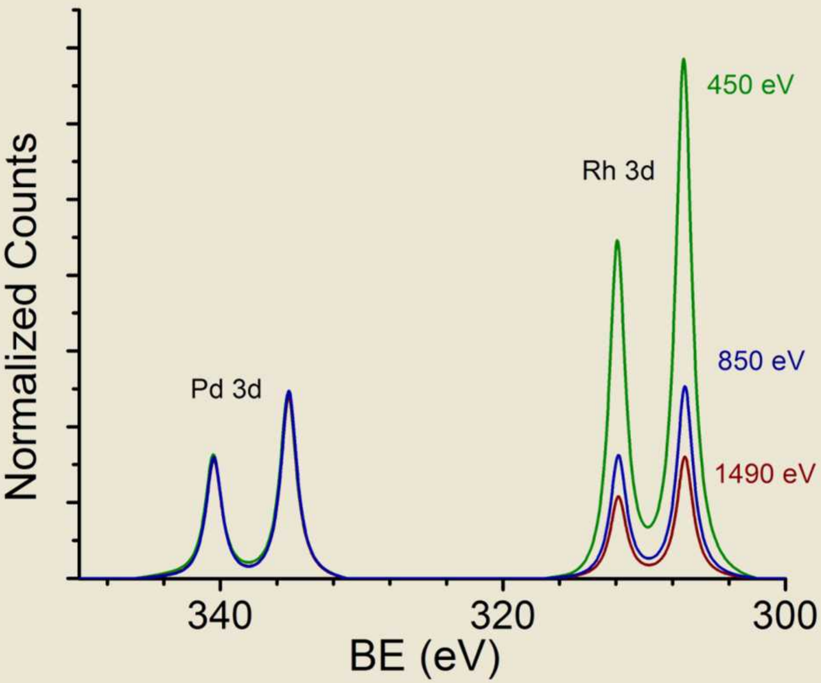
Higher energy photoelectrons travel farther

Lawrence Berkeley,
Advanced Light Source
Beamline 9.3.2

Energy Resolved Depth Profile (XPS)



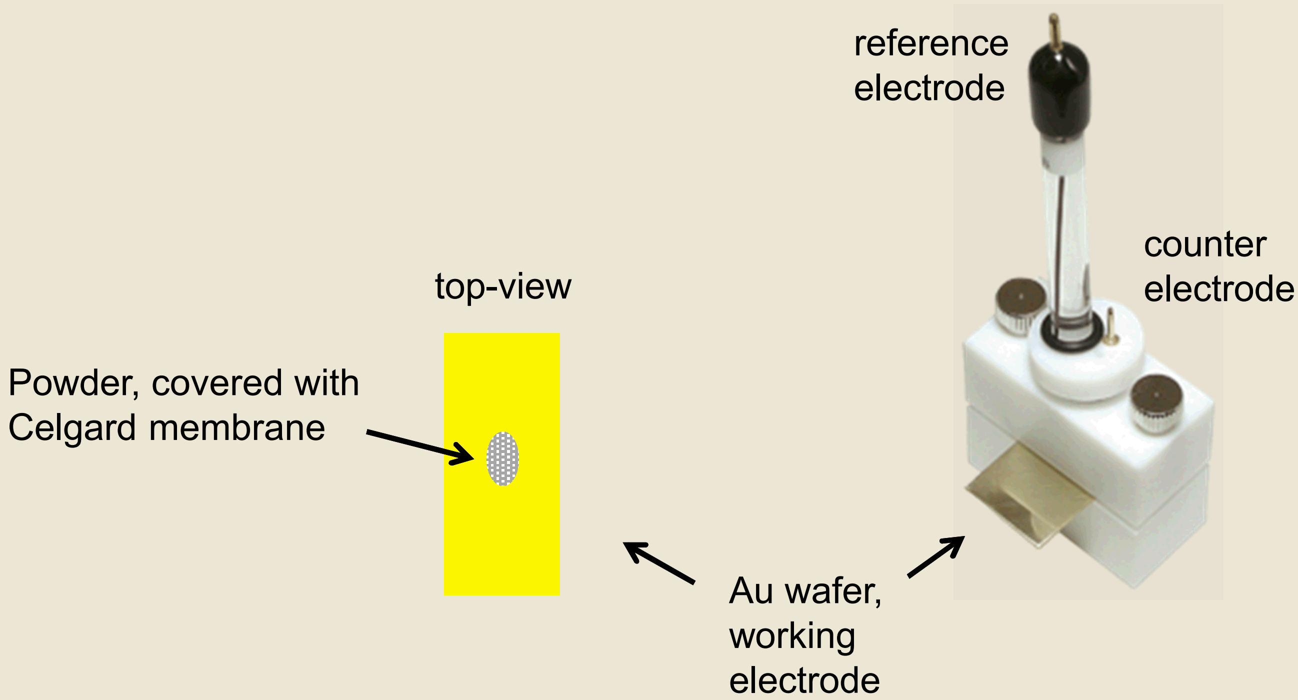
Spectra at three photon energies demonstrate surface Rh enrichment



Simulation:
4 - 8 Å adlayer, 25% bare Pd

Smekal, W. et *al*. Simulation of electron spectra for surface analysis (SESSA). Surf. Interface Anal. 2005, 37 (11), 1059-1067

Direct measurement of hydrogen desorption on powders



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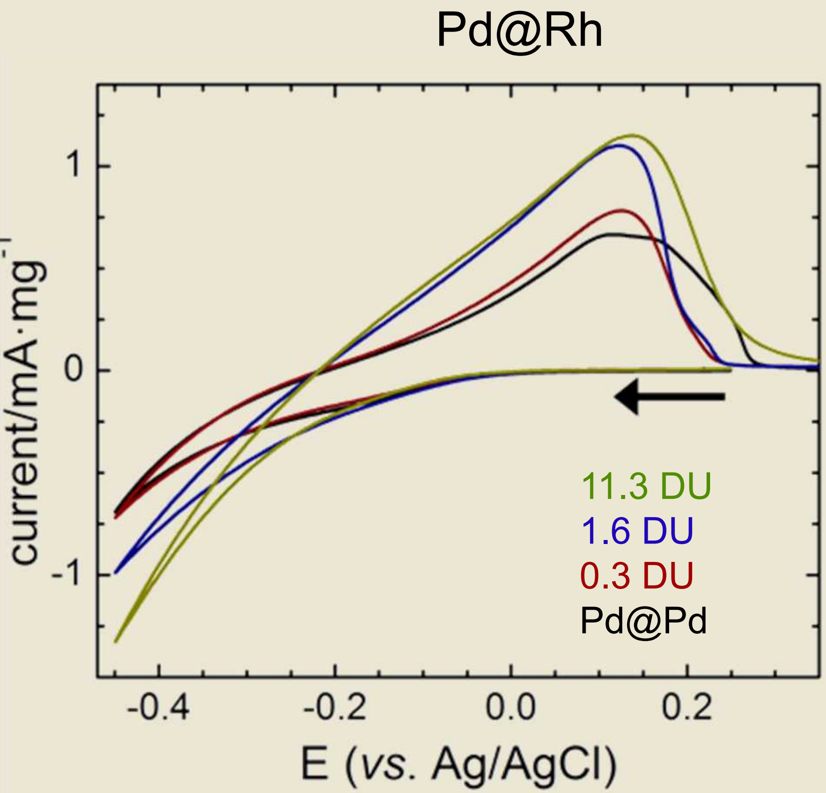

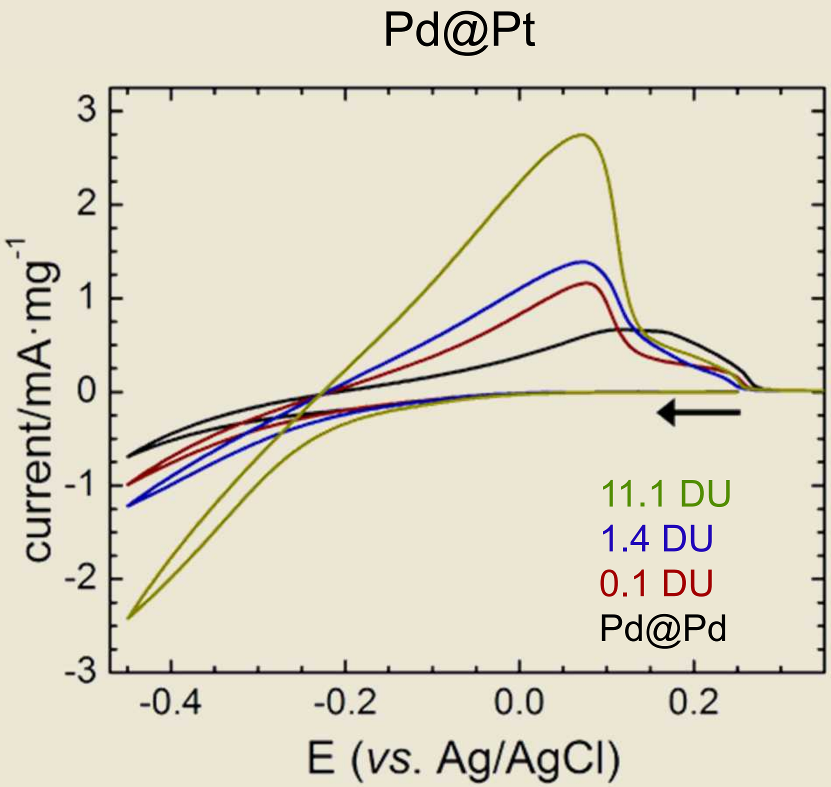

- Adlayer improves hydrogen absorption and desorption kinetics
- Greater effect with thicker layer

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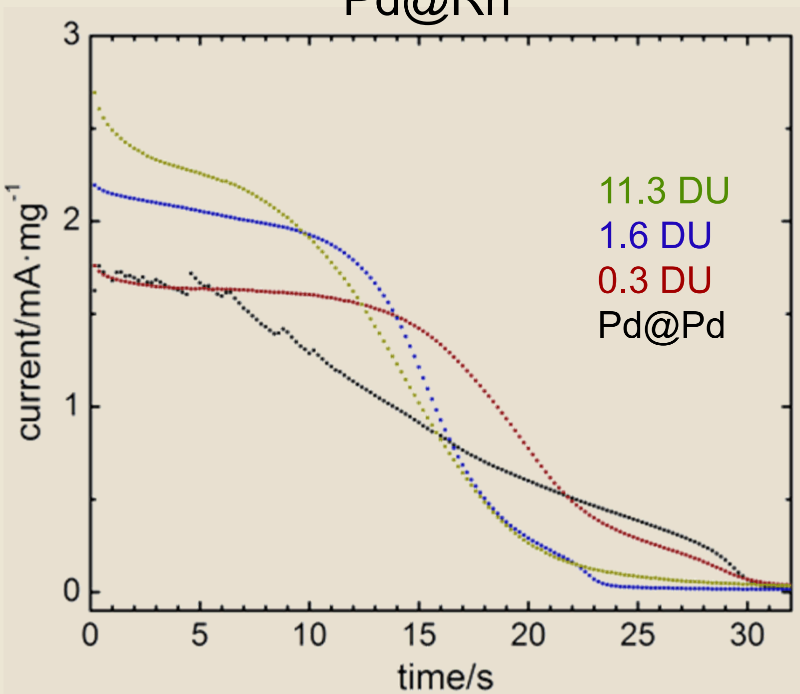
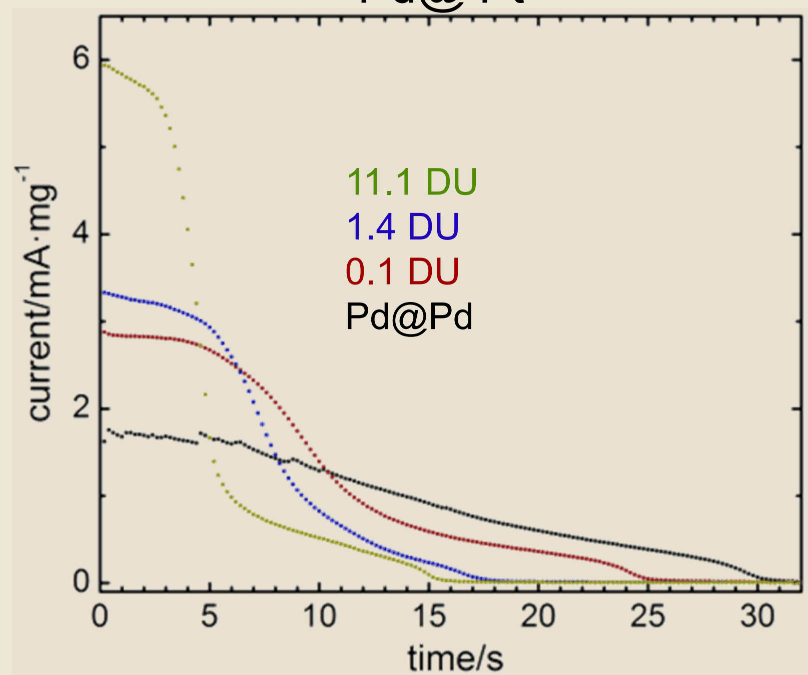
Direct measurement of hydrogen desorption on powders

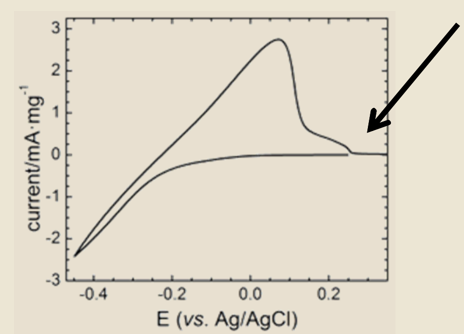
Pd@Rh



Pd@ Pt



- Powders charged with H_2 by applying 1.5 mA for 60s
- Poised at 0.27 V vs. Ag/AgCl to desorb hydrogen (t_0)



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