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Atomic-Layer Electroless Deposition on Noble Metal Powders

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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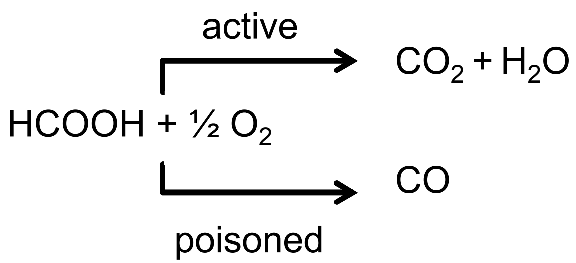
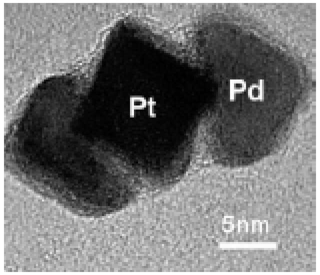
Bimetallic catalysts show enhanced properties – literature examples

Electro-oxidation of formic acid on Pt catalyst





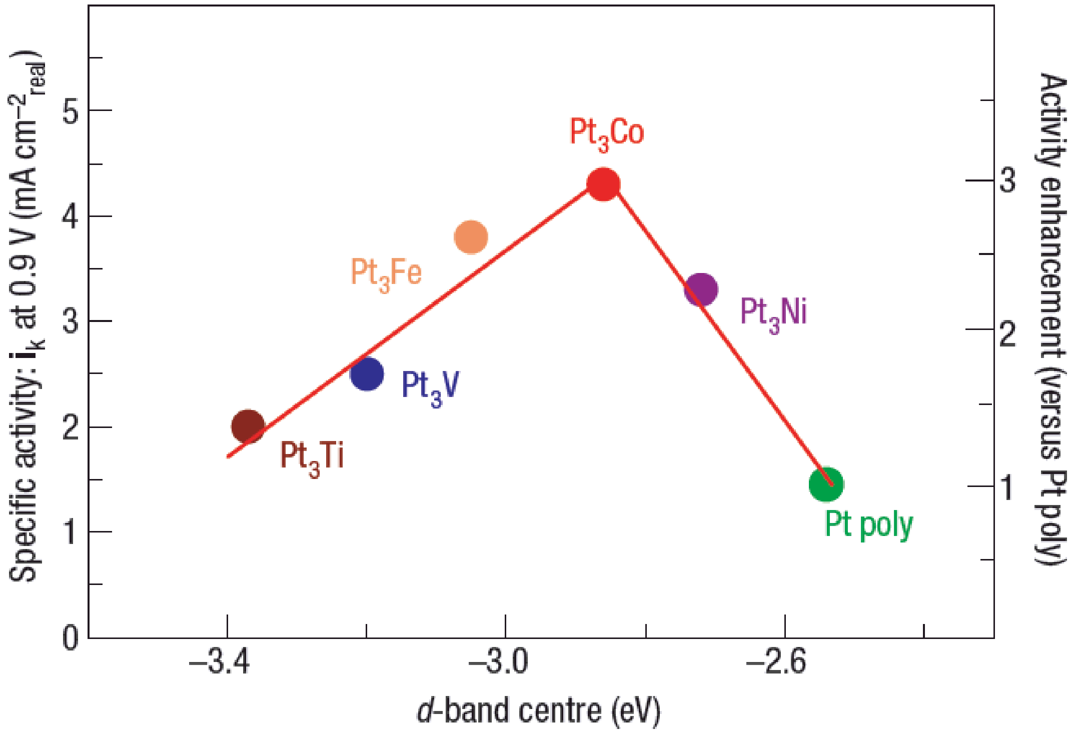
- Adlayers such as Bi, Sb, As, Pd favor active pathway (reduce poisoning)

H. Lee, S. E. Habas, G. A. Somorjai, P. Yang, J. Am. Chem. Soc. 2008, 130, 5406-5407

Bimetallic catalysts show enhanced properties – literature examples

Oxygen reduction reaction on
with bimetallic Pt catalysts

$\frac{1}{2} O_2 + 2 H^+ + 2 e^- \rightarrow H_2O$

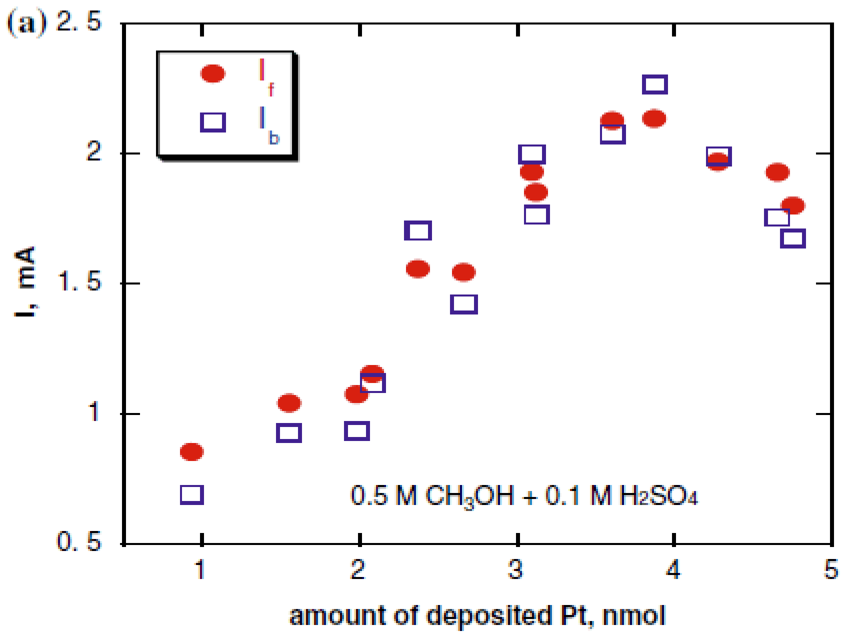


V. R. Stamenkovic et al., Nature Materials, 2007, 6, 241-247

Adsorbed layers (adlayers) on catalysts show enhanced properties – literature example

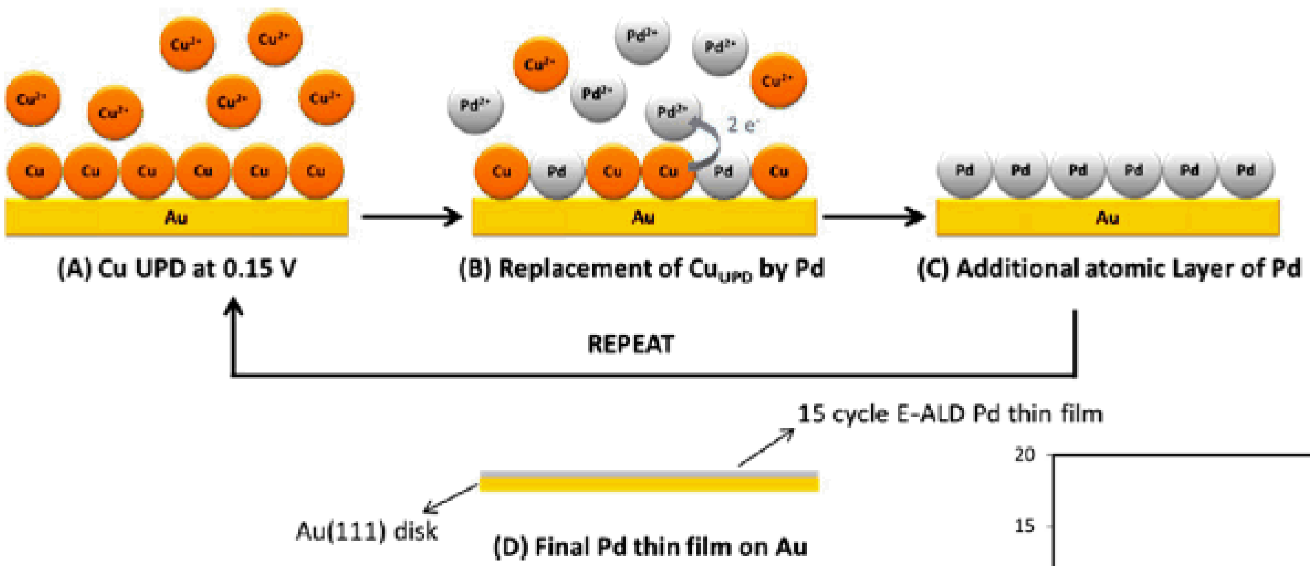
Methanol oxidation reaction on with Pt monolayer catalysts (4 nmol = 0.8 ML on Ru)

$CH_3OH + H_2O \rightarrow CO_2 + 6\ H^+ + 6\ e^-$

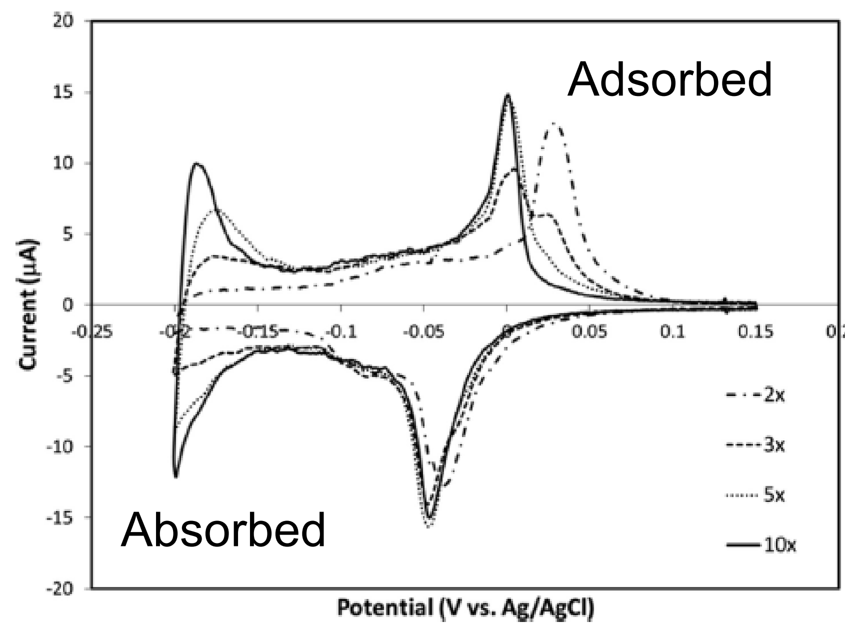


R. R. Adzic et al., Topics in Catalysis 2007, 46, 249-262

Electrochemical Atomic Layer Deposition (E-ALD)



0.28 cm^2
10 mV/s
0.1M H_2SO_4

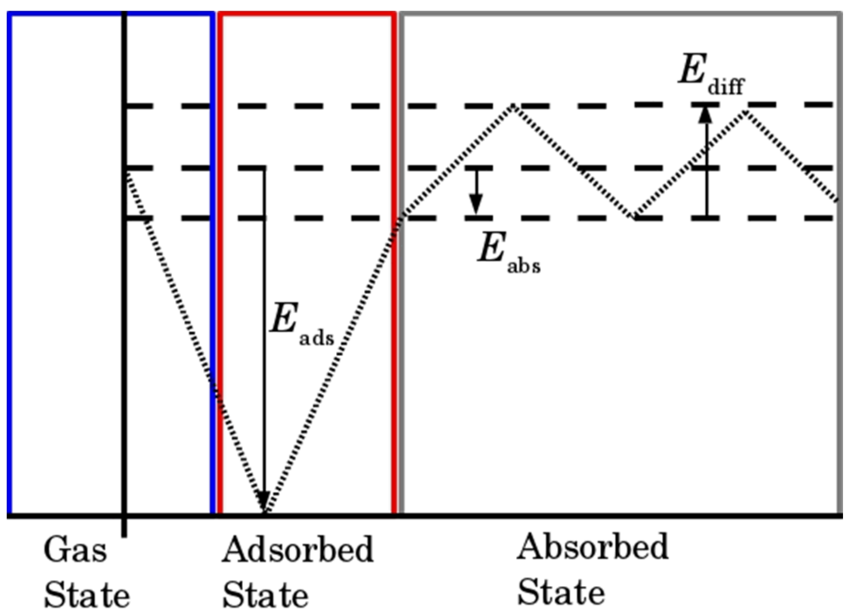


L. B. Sheridan et al., J. Phys. Chem. C 2013, 117, 15728

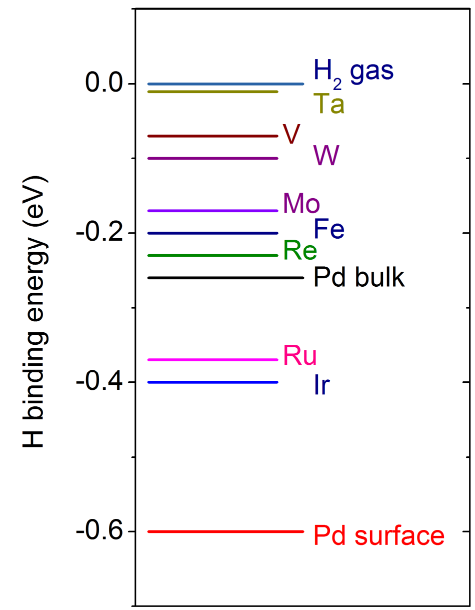
Surface modification should improve kinetics of hydriding and dehydriding Pd

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

- Surface Pd-H is very stable
- High surface site occupancy
- Large activation barrier
- Near-surface alloys destabilize surface hydrides
- May then improve absorption kinetics

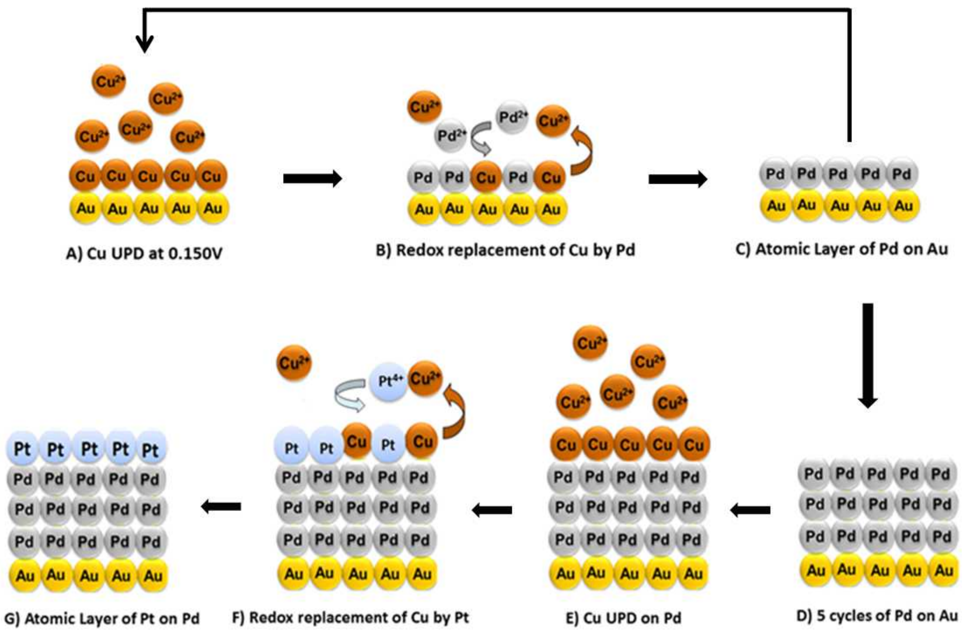


M. Salloum, S.C. James, D. B. Robinson. Chem Eng Sci. 2014 10.1016/j.ces.2014.09.001



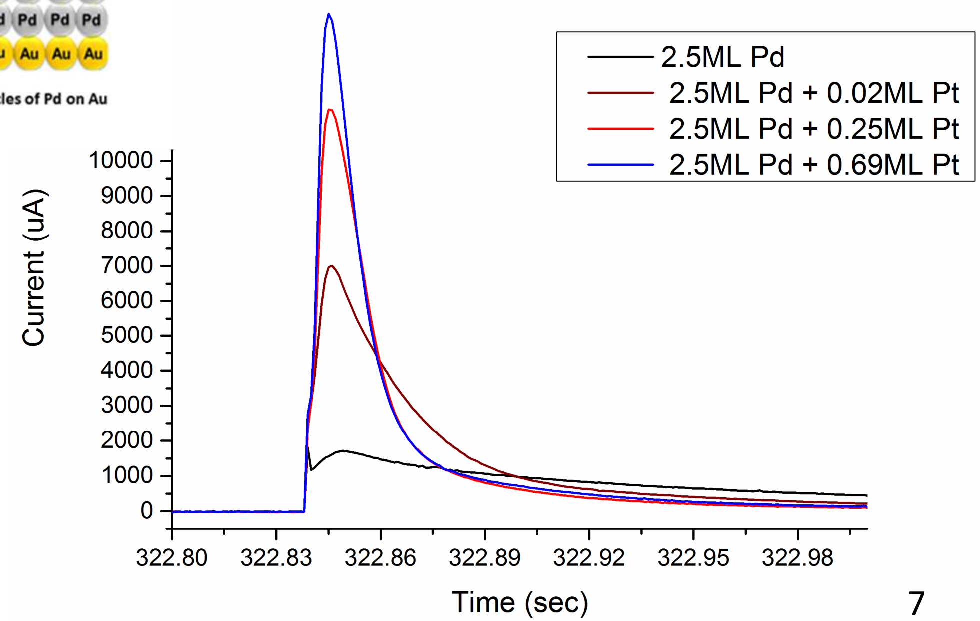
J. Greeley, M. Mavrikakis. J. Phys. Chem. B 2005, 109, 3460-3471

E-ALD: Pt on Pd

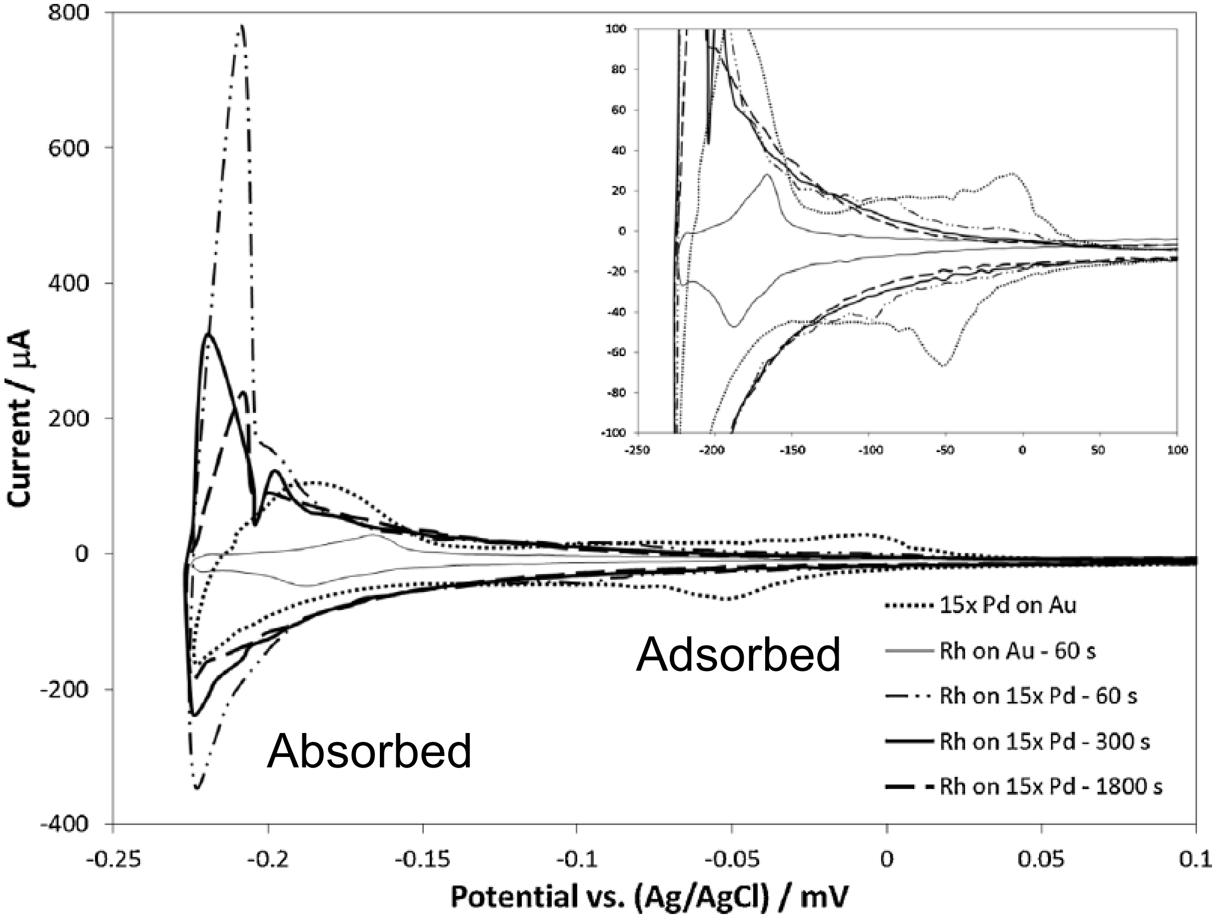


-250 to 0 mV
0.1M H_2SO_4
0.7 cm^2

A tiny amount of Pt on Pd enhances H uptake and release



E-ALD: Rh on Pd

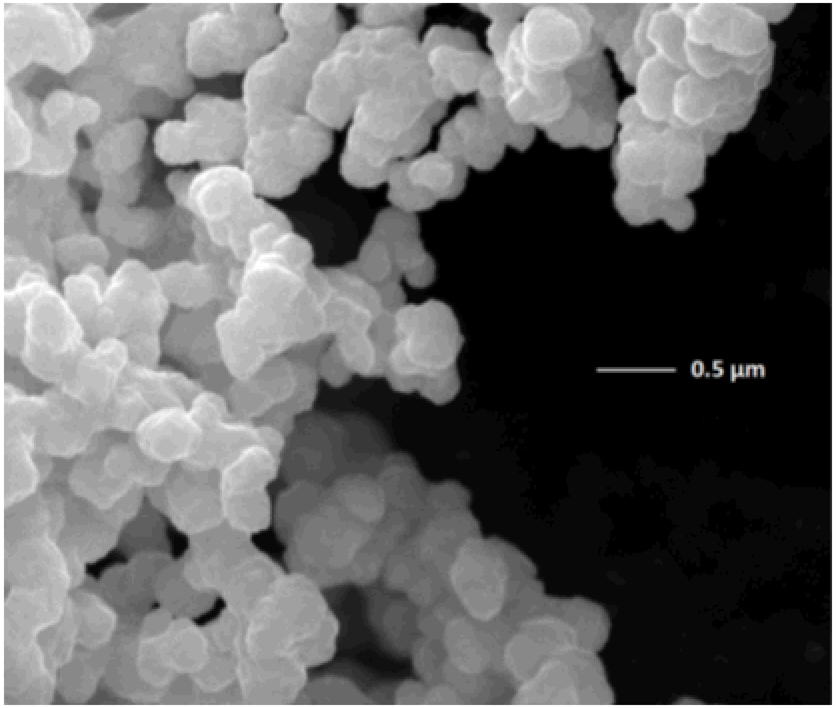


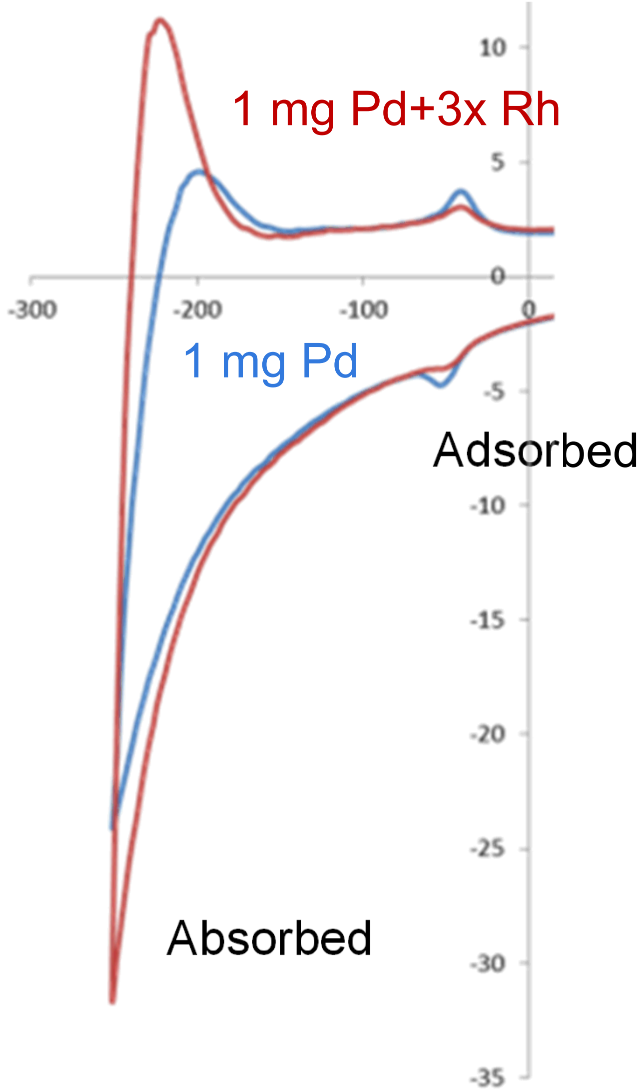
2.1 cm^2
10 mV/s
0.1M H_2SO_4

Rh layers also enhance kinetics

L. B. Sheridan et al., Electrochim. Acta 2014, 128, 400-405

Rh on Pd: E-ALD on powders

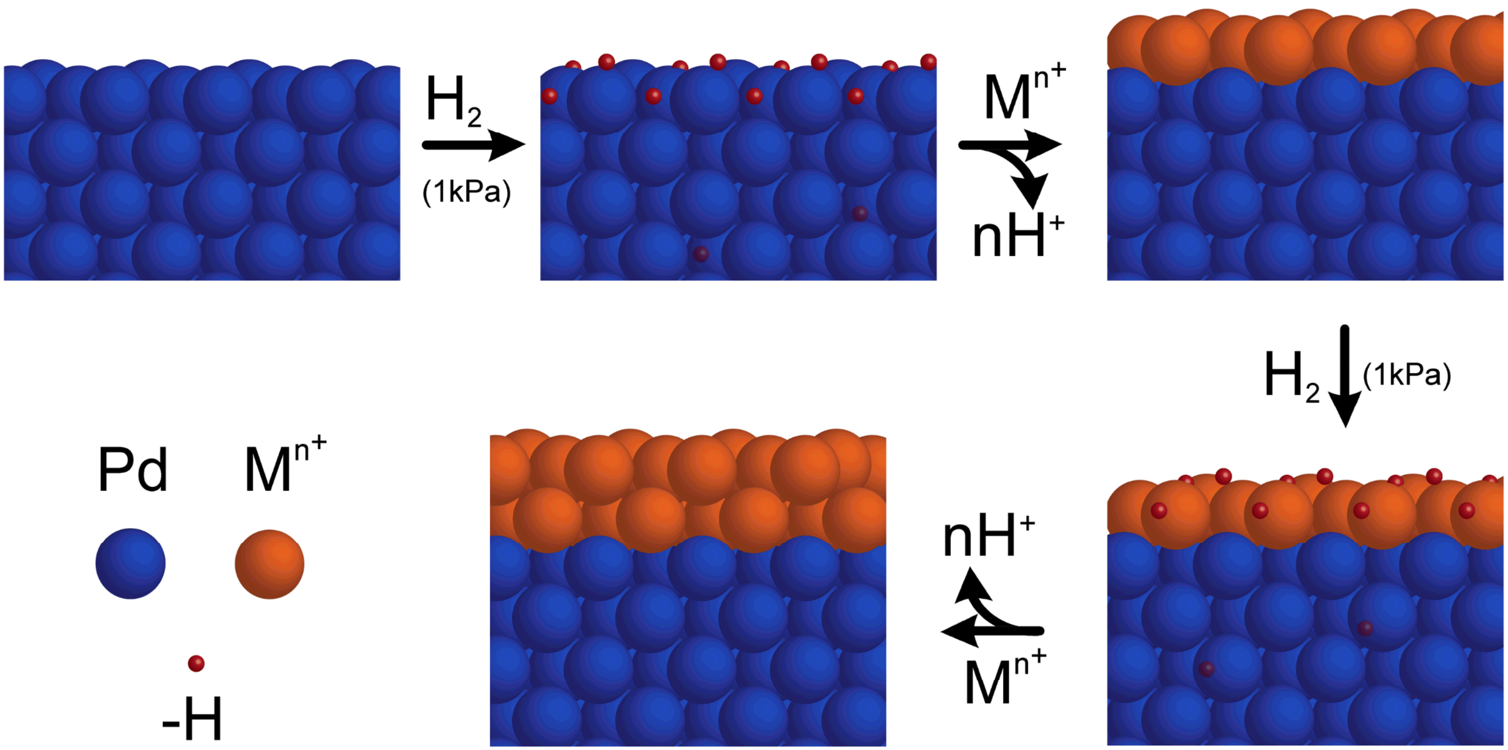




Process applies to powders

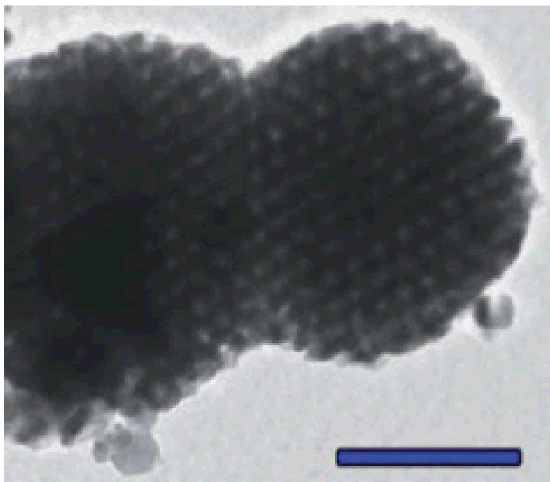
- Kinetic enhancement still works
- Large counterelectrode needed

Atomic-Layer Electroless Deposition (ALED)

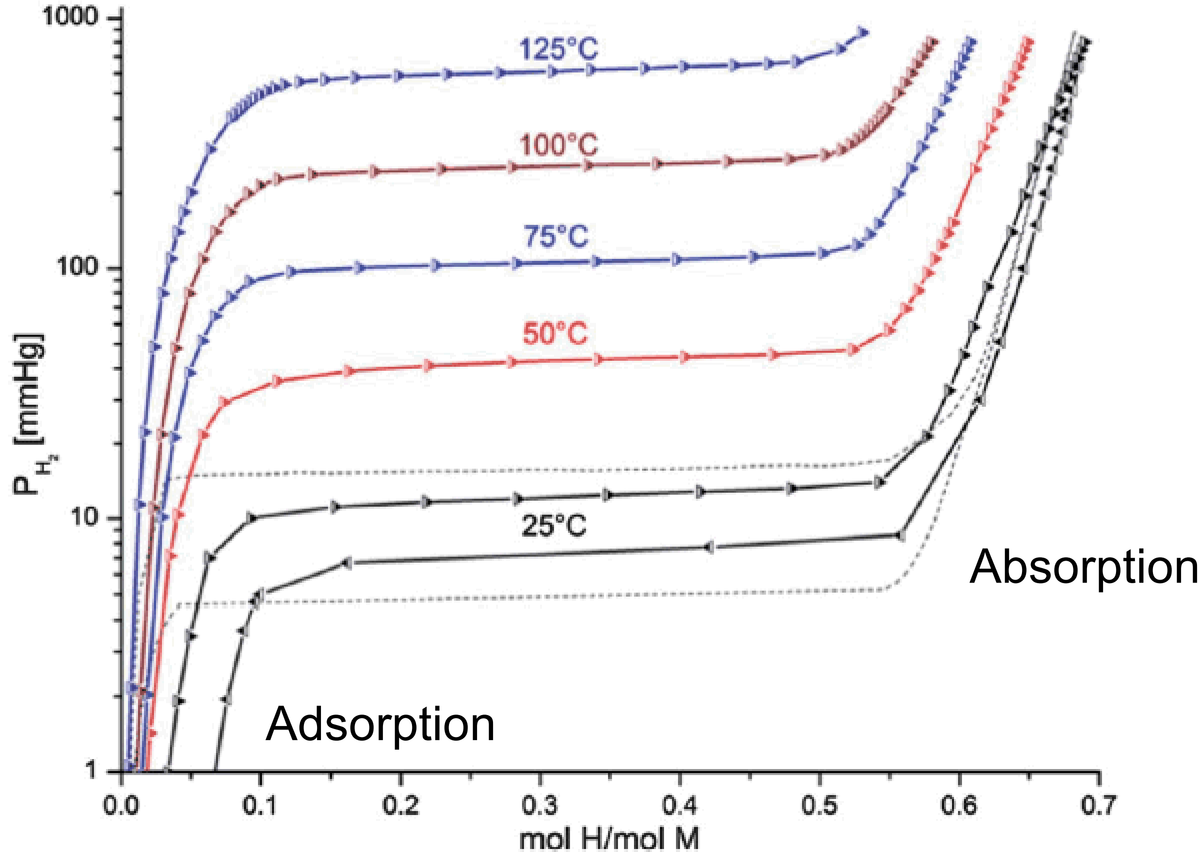


Scalable, room temperature, works with insulating support, applies to “rough” surfaces with high surface area

Absorption of H_2 gas by Pd



100 nm

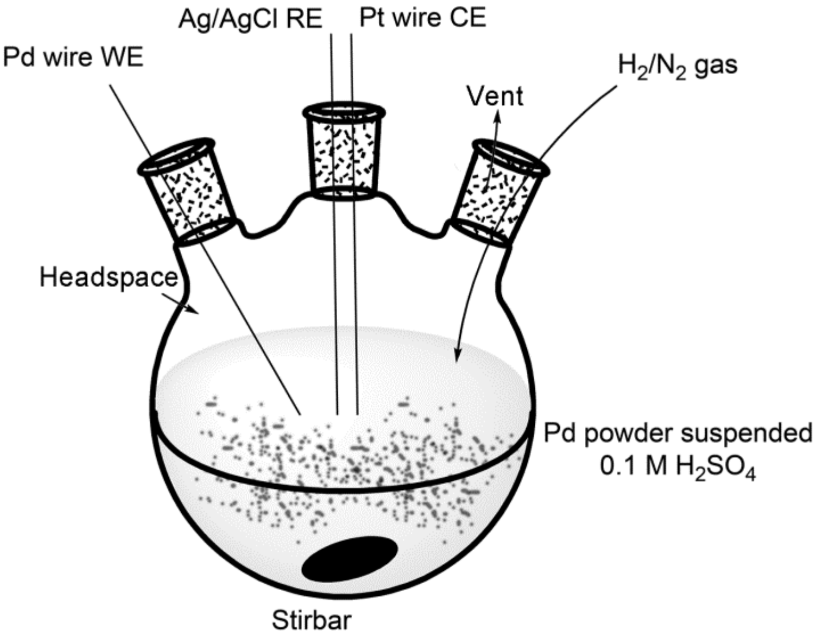


P. J. Cappillino et al.,
J. Mater. Chem. A 2013, 1, 602.

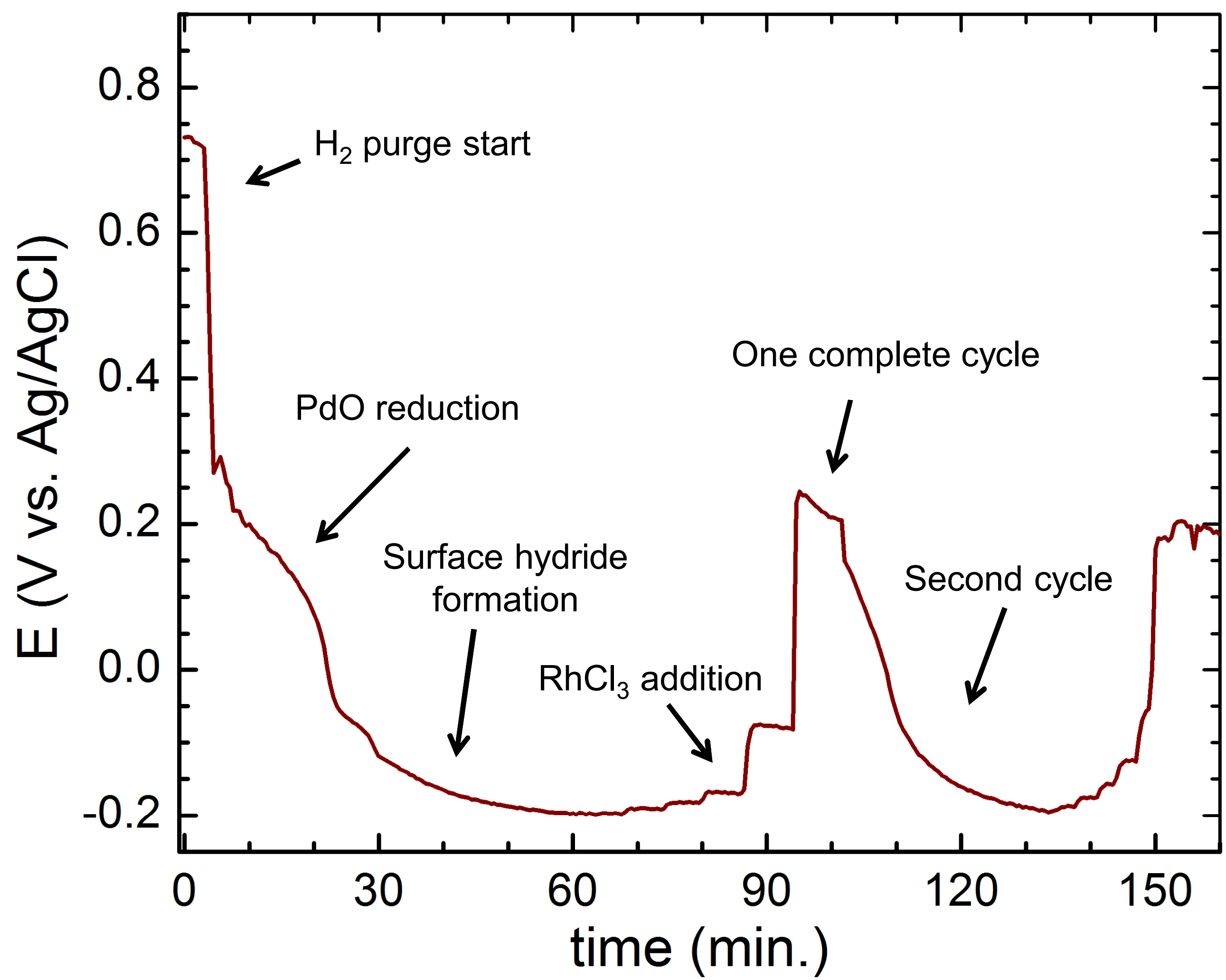
Only surface, dilute bulk hydride
below a transition pressure

Simple Apparatus for ALED

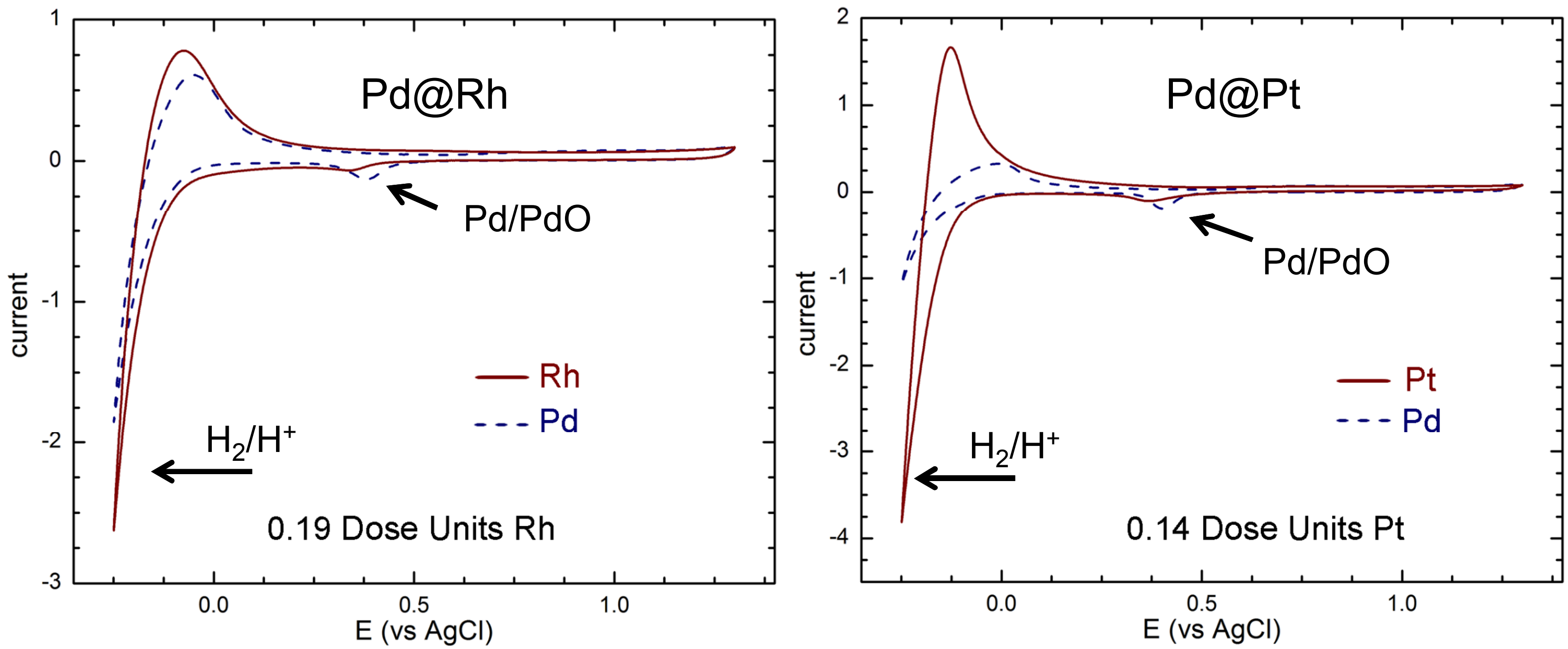
- Pd powder suspended in electrolyte
- Reagent gas (1% H_2/N_2)/inert gas source
- Metal salt added by syringe
- Electrodes to measure progress of reaction



Monitor open circuit potential to follow reaction

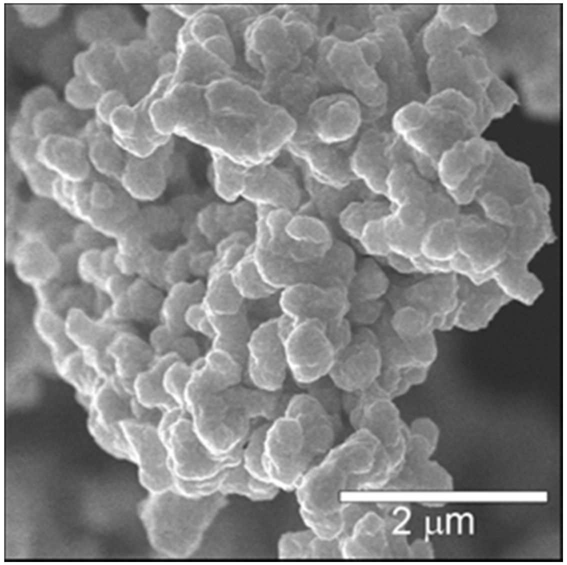


Cyclic voltammetry of Pd test wire before and after deposition of adlayer of Rh (left) and Pt (right)

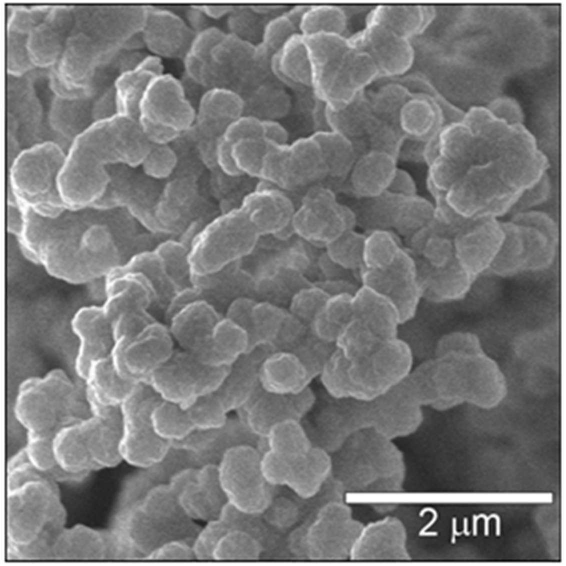


CV shows that adlayer blocks Pd/PdO redox couple and suggests improved hydride/dehydride kinetics

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



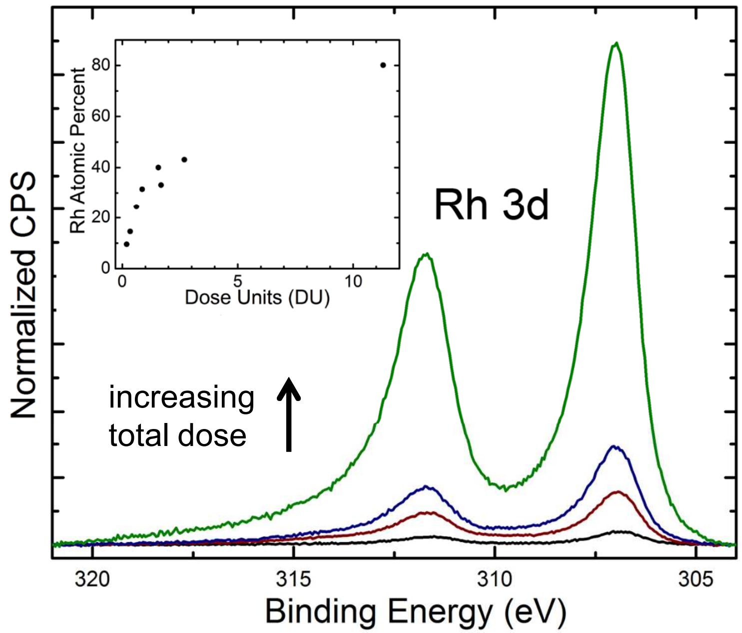
Pd powder before deposition



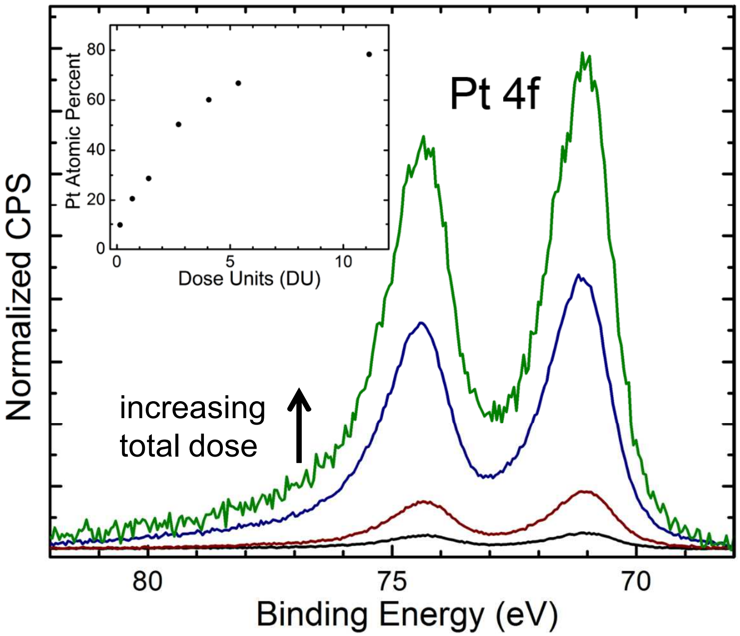
Pd powder after 2 cycles of ALED

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

Pd@Rh



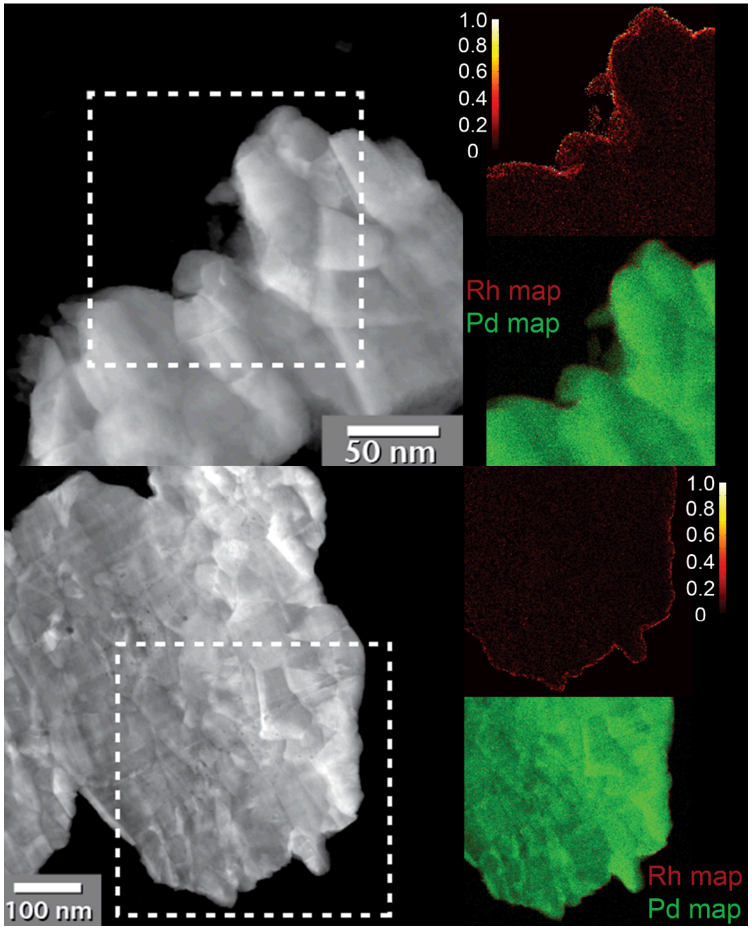
Pd@Pt



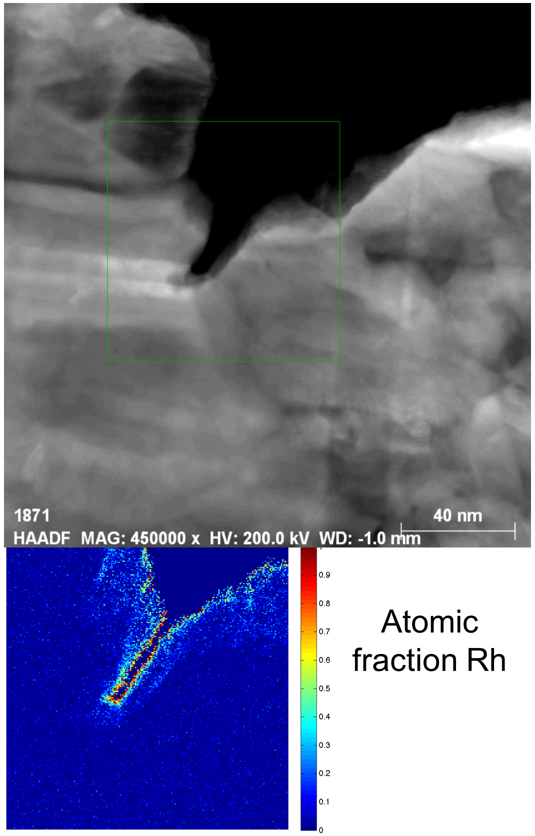
Rh and Pt peaks normalized to Pd peak at 335 eV

STEM-EDS demonstrates conformal coating on Pd@Rh, 2 cycles

Atomic fraction Rh



Atomic fraction Rh



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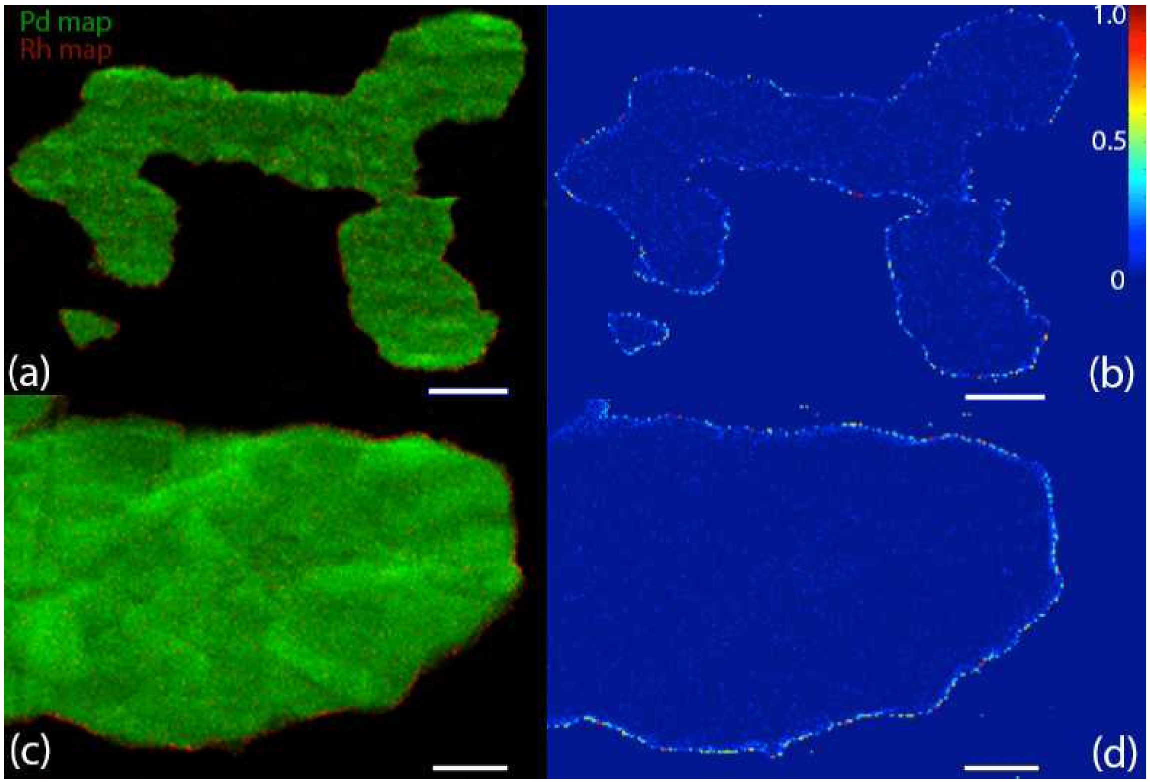
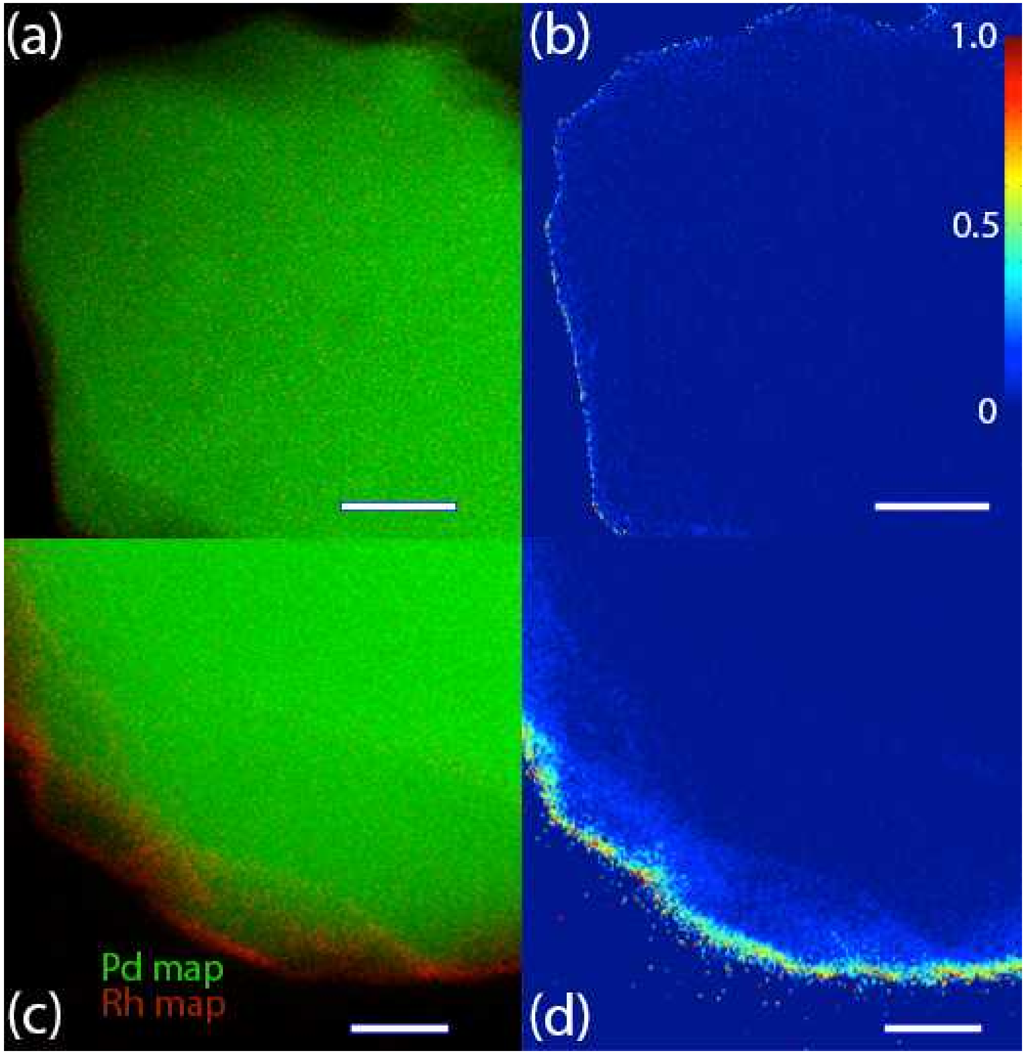


Atomic fraction Rh

250 nm

60 nm

STEM-EDS demonstrates conformal coating on Pd@Rh, 1 cycle

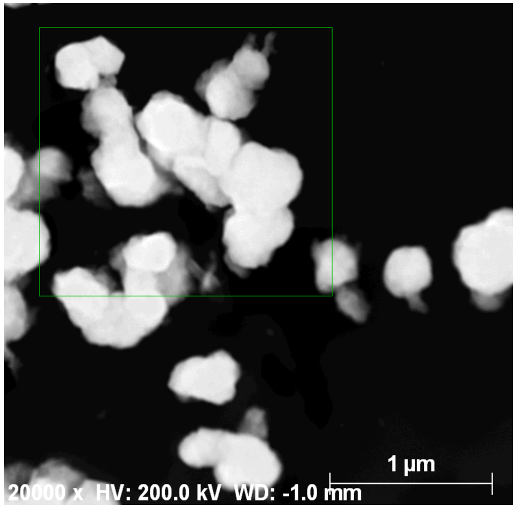


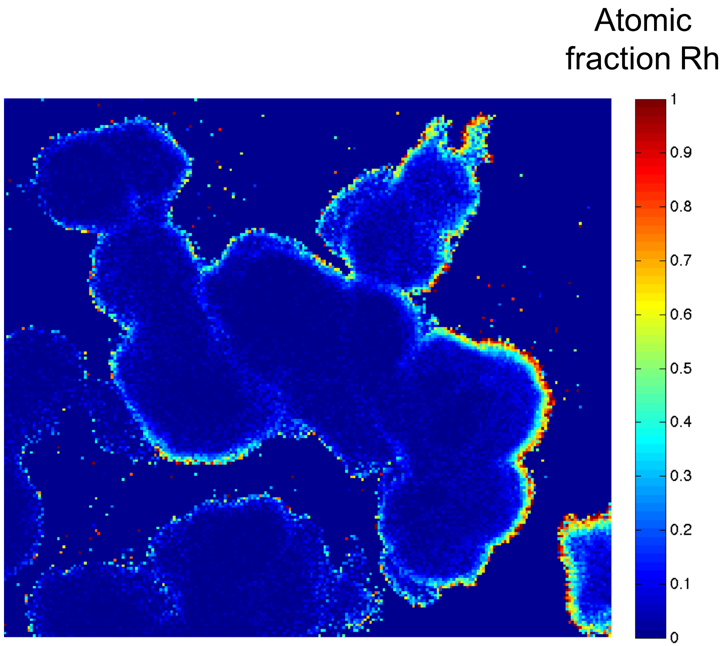
Atomic fraction Rh

50 nm

20 nm

STEM-EDS demonstrates conformal coating on Pd@Rh, 8 cycles as well, some thickness variation





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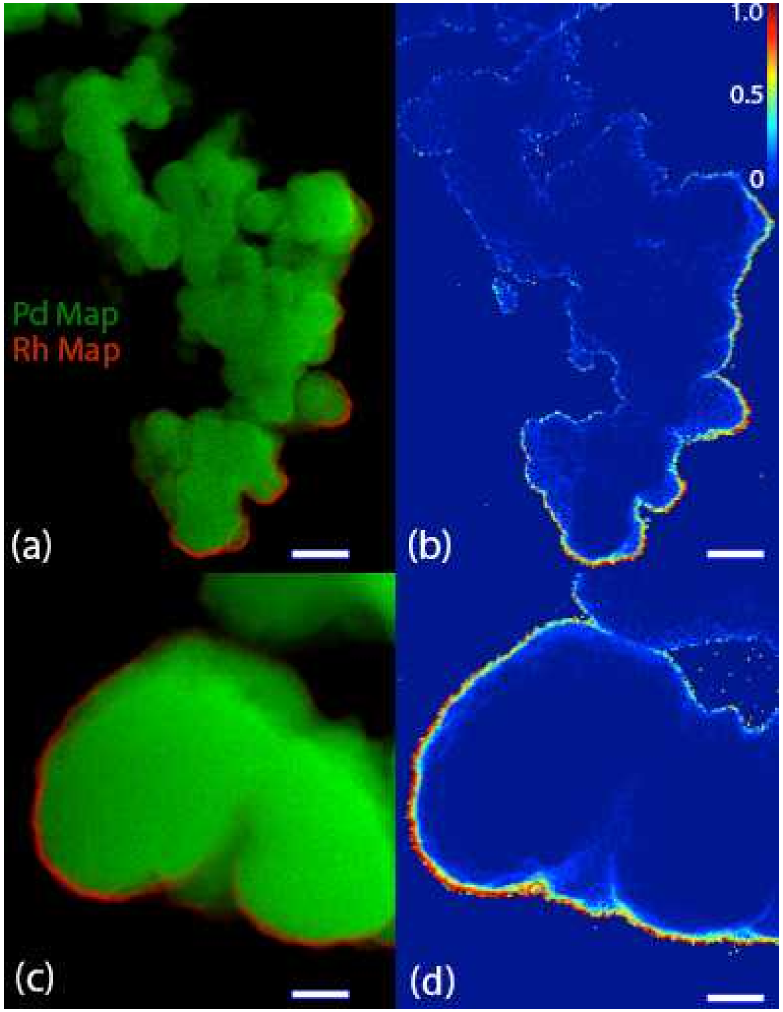
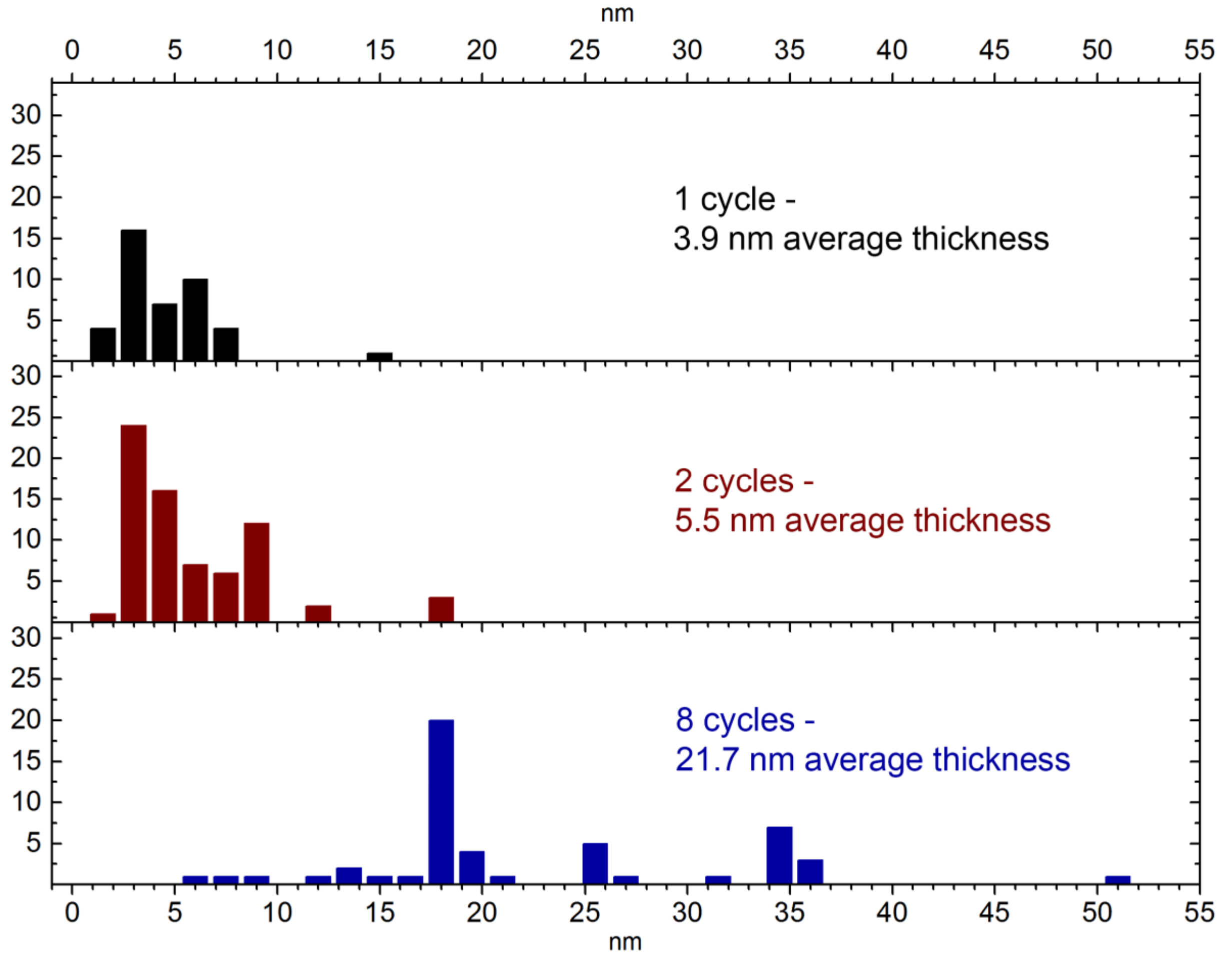


Atomic fraction Rh

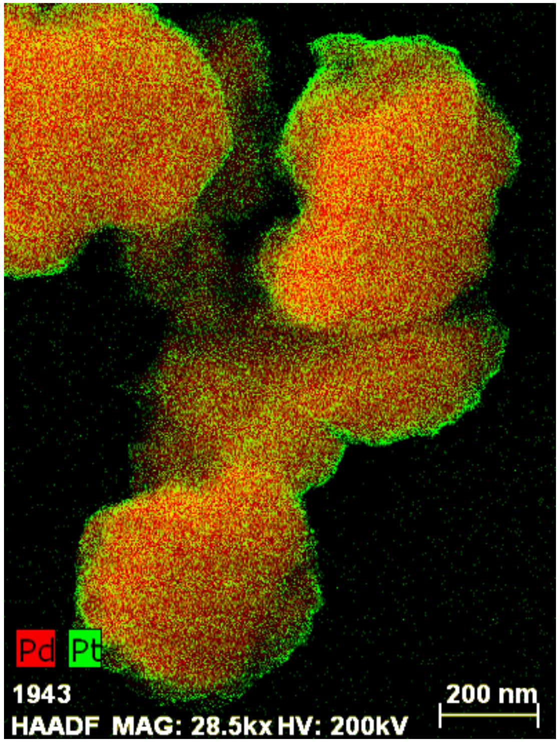
500 nm

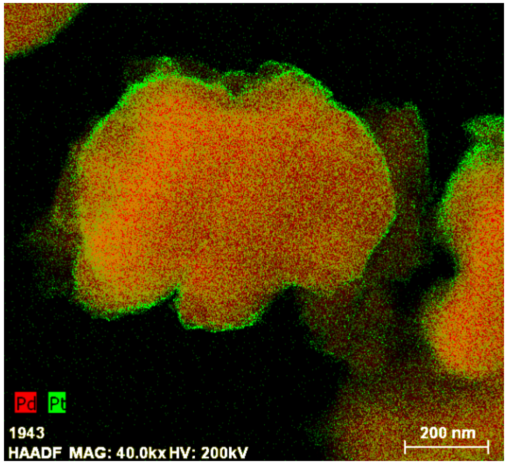
150 nm

Thickness histogram



STEM-EDS demonstrates conformal coating on Pd@Pt, 1 cycle

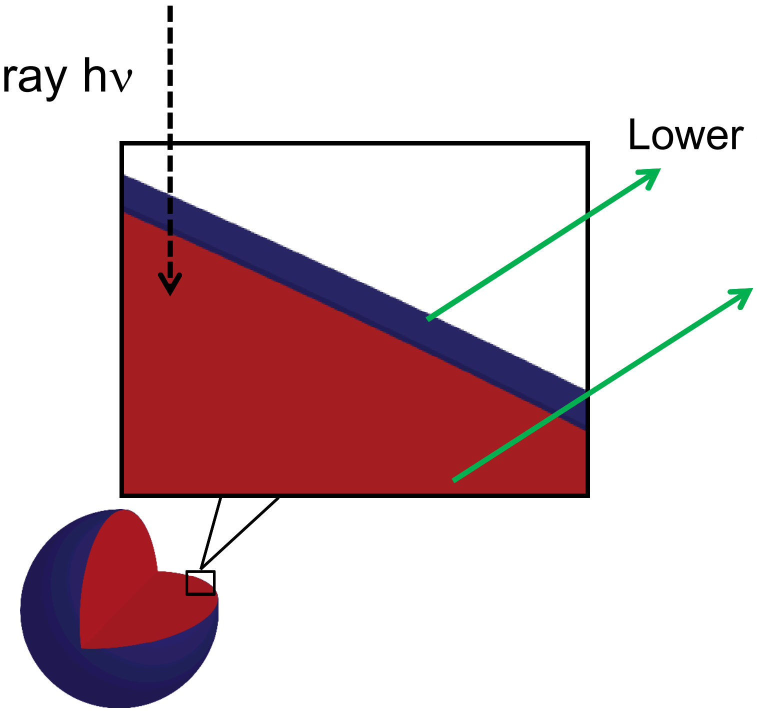




Energy Resolved Depth Profile (XPS)

At synchrotron, incident photon energy (hν) can be tuned, KE = hν - BE

X-ray hν

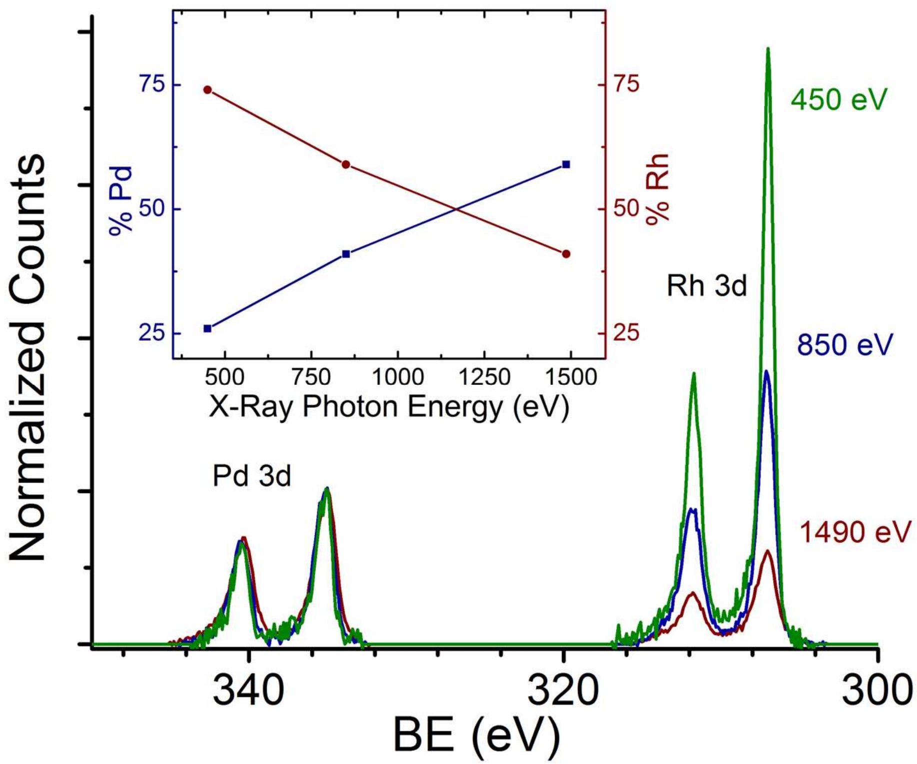


Lower energy photoelectrons are more surface sensitive

Higher energy photoelectrons travel farther

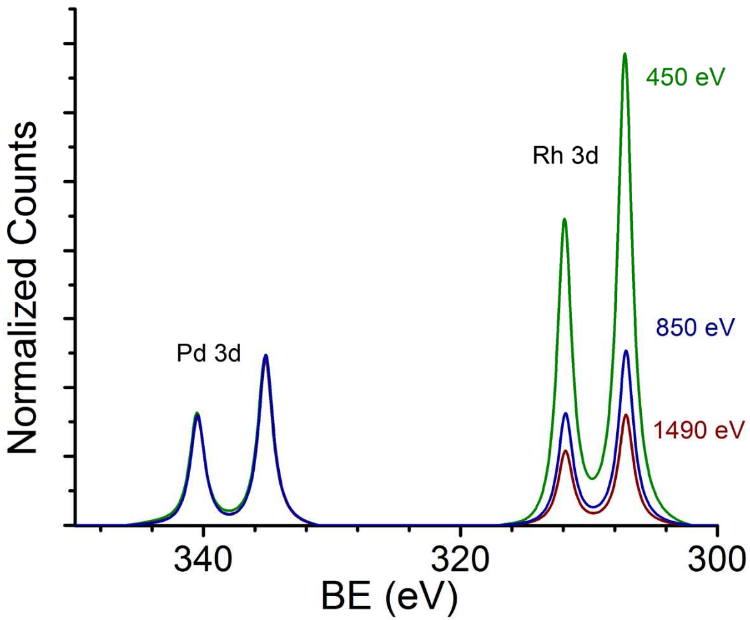
Lawrence Berkeley,
Advanced Light Source
Beamline 9.3.2

Energy Resolved Depth Profile (XPS)



Spectra at three photon energies demonstrate surface Rh enrichment

Some 3D growth and bare Pd indicated by simulated XPS depth profile

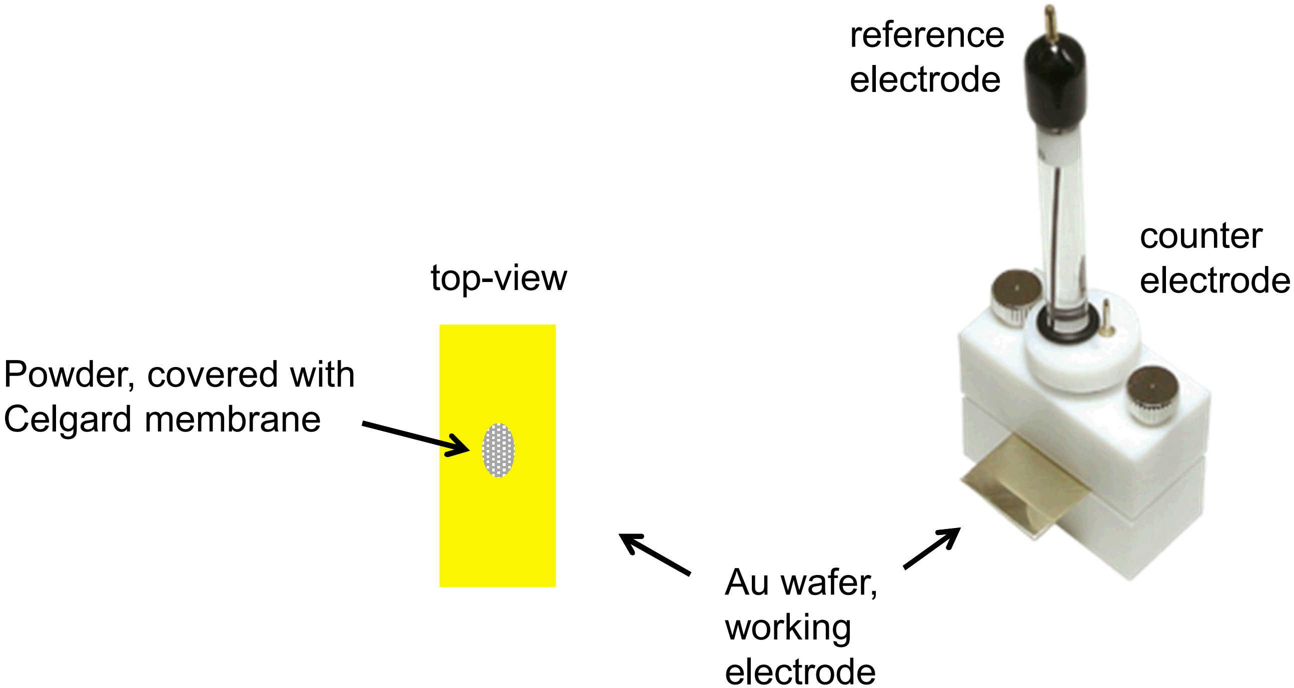


RMS Error in Rh atom % between experiment and simulation			
Pd	**4 Å layer**	**8 Å layer**	**RMSE**
0.24	-	0.76	3.6
0.23	0.05	0.72	3.8
0.23	0.07	0.70	4.0
0.21	0.14	0.65	4.3
0.14	0.46	0.40	6.7
0.05	0.95	-	11.4
-	1.00	-	11.8
-	-	1.00	19.4

Simulated* spectra with 4 & 8 Å Rh layers and 20 – 25% bare Pd

*Smekal, W. et *al*. Simulation of electron spectra for surface analysis (SESSA): a novel software tool for quantitative Auger-electron spectroscopy and X-ray photoelectron spectroscopy. Surf. Interface Anal. 2005, 37 (11), 1059-1067

Direct measurement of hydrogen desorption on powders



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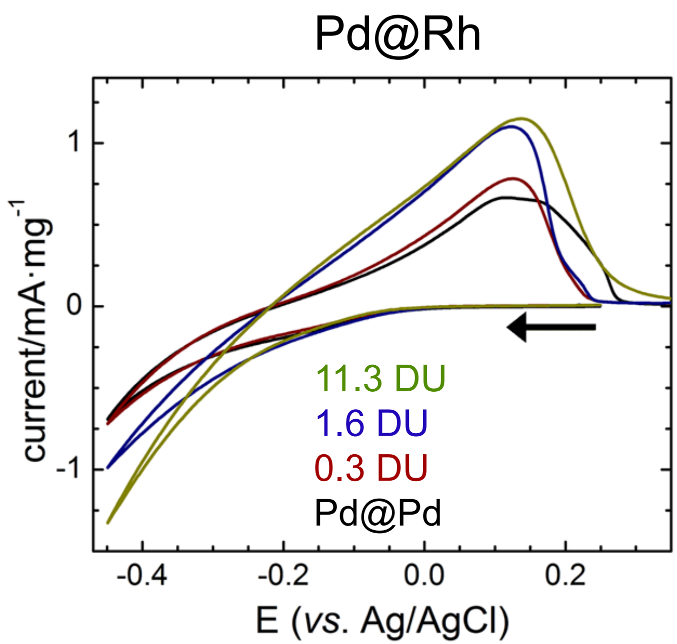
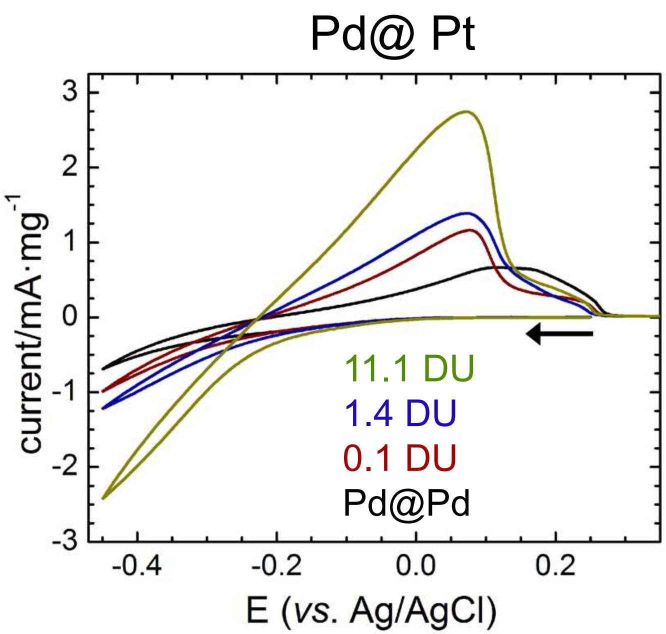
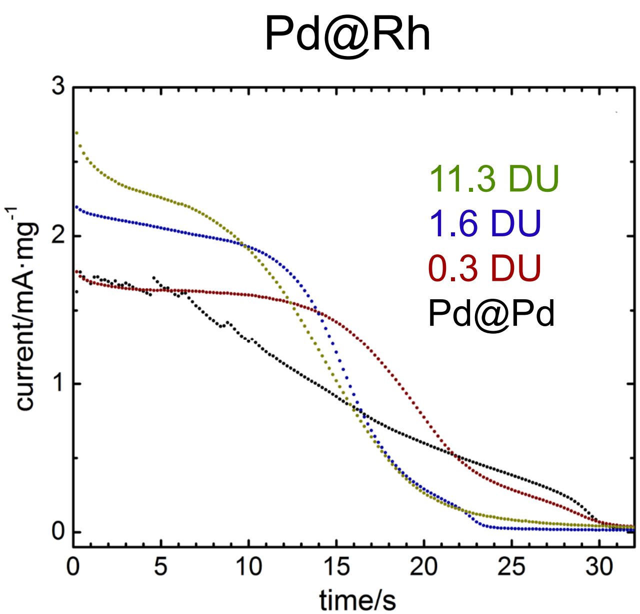
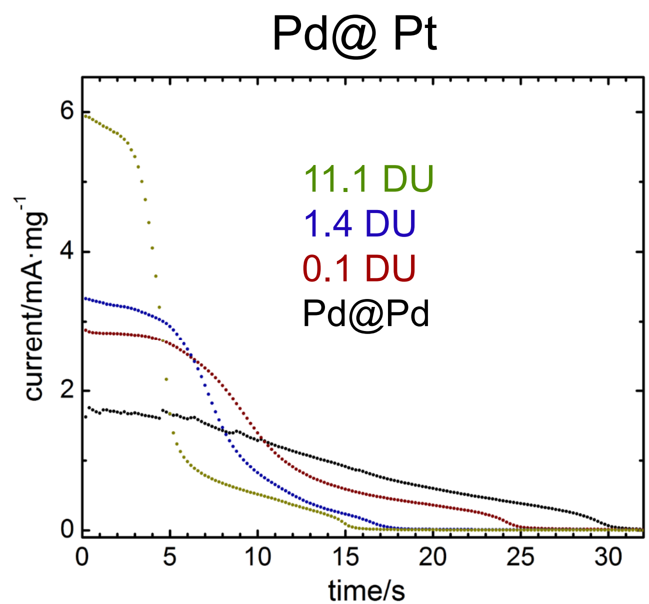




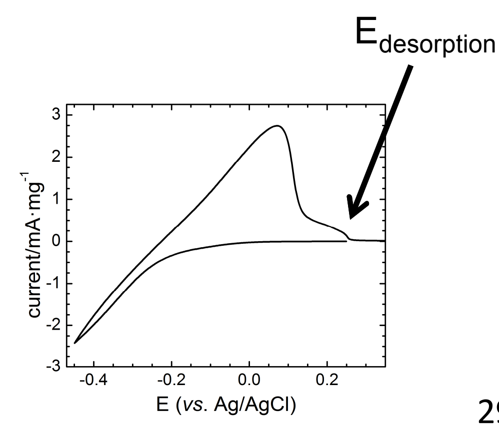
- Adlayer improves hydrogen absorption and desorption kinetics
- Greater effect with thicker layer

Direct measurement of hydrogen desorption on powders



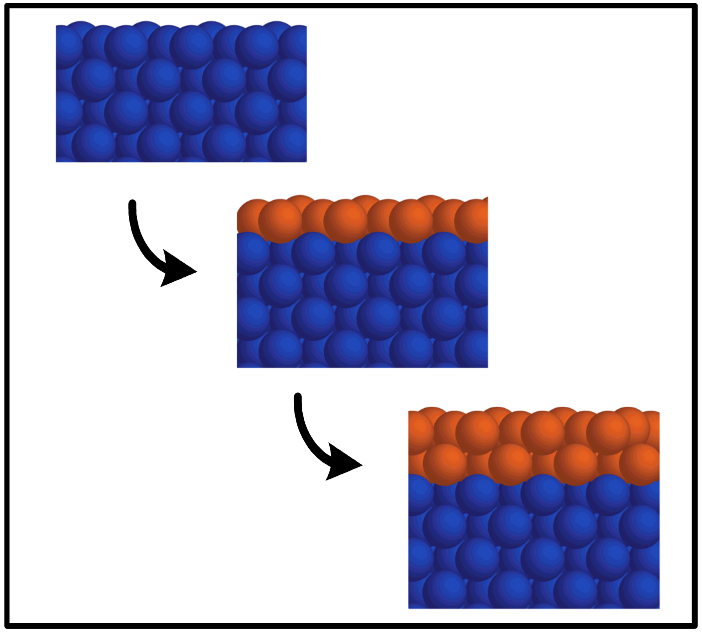


- Powders charged with H_2 by applying 1.5 mA for 60s
- Poised at 0.27 V vs. Ag/AgCl to desorb hydrogen (t_0)



Summary

- New strategy for large-scale deposition of adlayers on high surface area powders (Pd/C works too!)
- STEM-EDS shows a conformal adlayer can be formed
- STEM-EDS and ERXPS suggest nanometer-scale adlayers
- Powders show improved hydrogen adsorption and desorption kinetics



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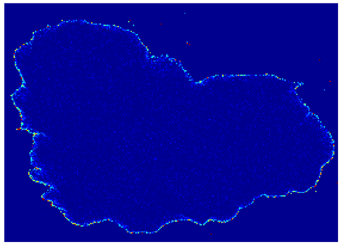

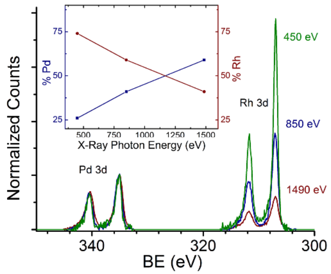

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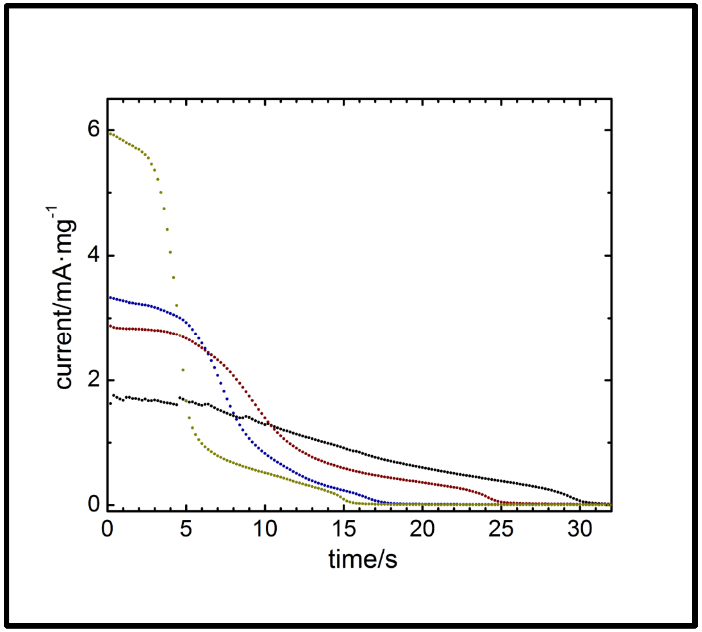
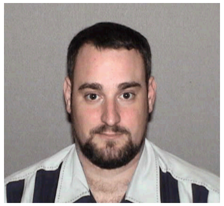
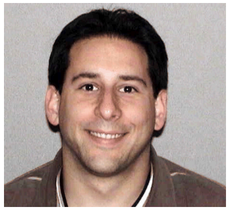


Acknowledgements



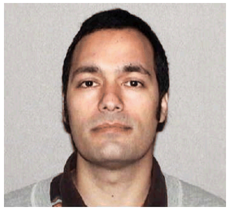
Patrick Cappillino
ALED
Now at UMass-Dartmouth



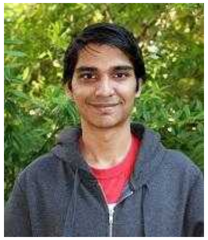
Josh Sugar
STEM-EDS

David Benson
Powder E-ALD
U. of Georgia

Professor John Stickney
E-ALD
U. of Georgia



Farid El Gabaly
XPS



Kaushik
Jagannathan
E-ALD kinetics
U. of Georgia

Maher Salloum
Theory/modeling

Leah Sheridan
E-ALD films
Now at Ametek

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Patrick J. Cappillino et al., Langmuir 30 (16) 4820-4829, Apr 2014.
http://dx.doi.org/10.1021/la500477s