Advanced Electrocatalysts for PEM Fuel Cells

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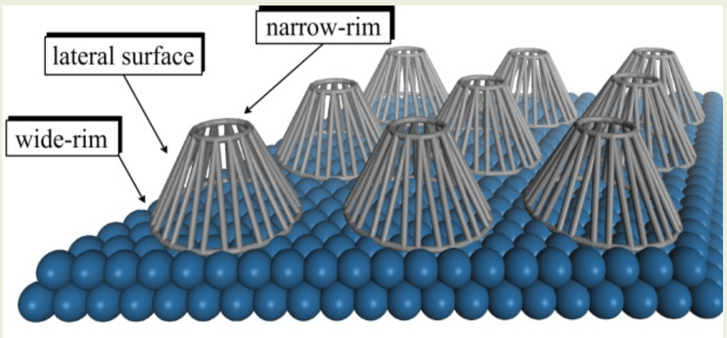

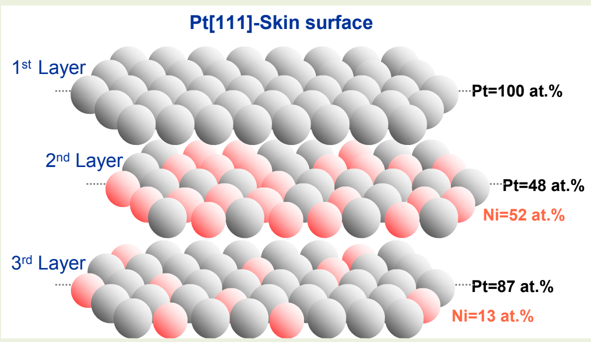

DOE Webinar on PEM Fuel Cells 2-12-2013

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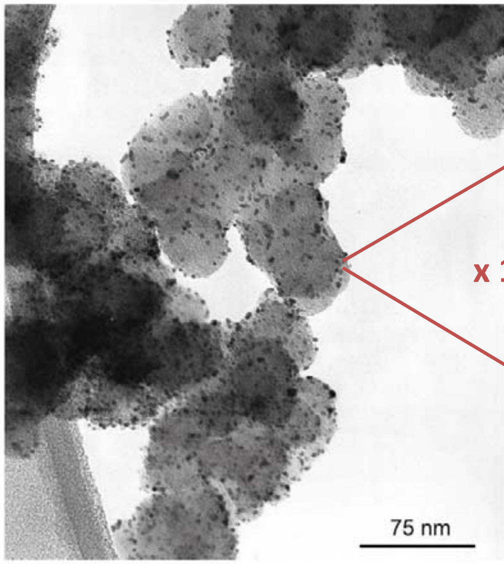
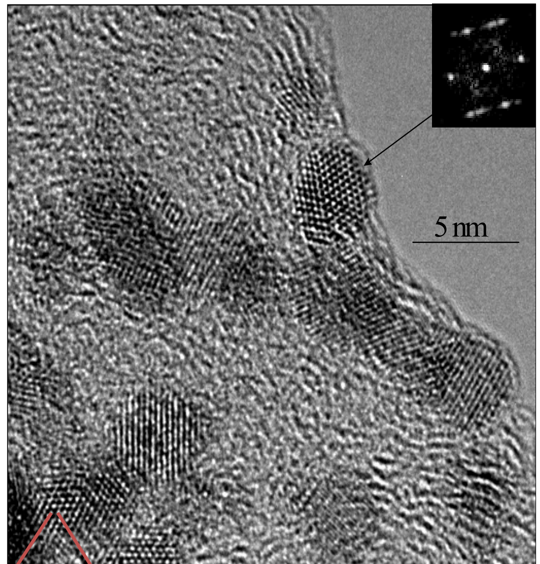
HR-TEM: *Characterization of Nanoscale Pt/C Catalyst*



x 15



Shape

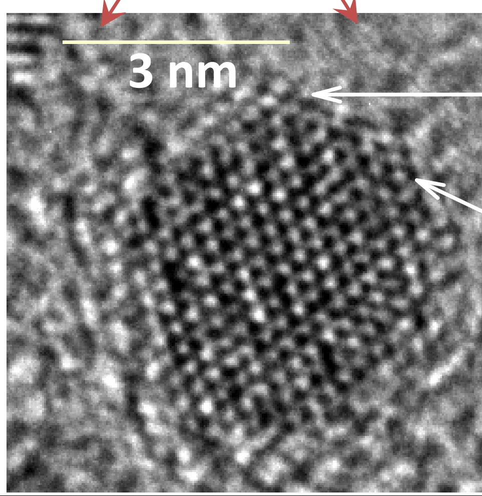
Size distribution **c-15 nm**

Bulk composition

Surface composition ?

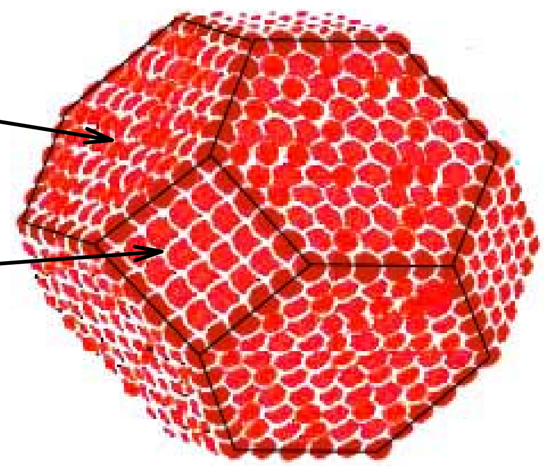
Surface structure ?

x 5



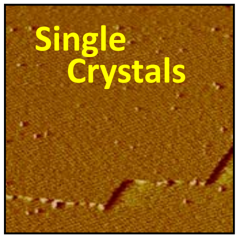
(111)

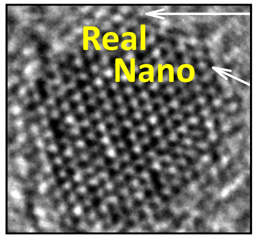
(100)



Surface Science Approach

MATERIALS-BY-DESIGN





METALS

M -OXIDES

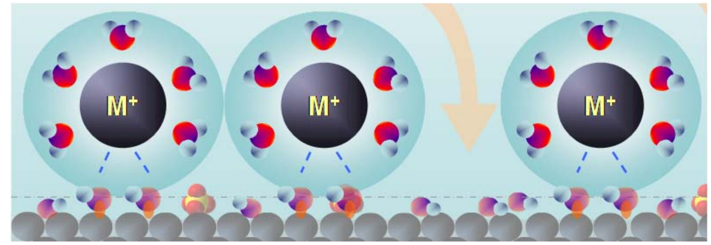
OXIDES

DOUBLE-LAYER-BY-DESIGN

ANIONS

SOLVENT

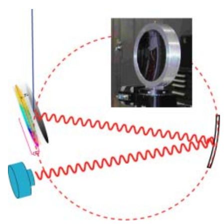
CATIONS



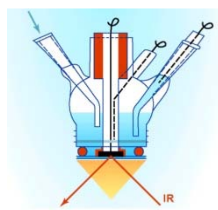
design, synthesis, characterization, and testing of well-defined interfaces

Surface Characterization

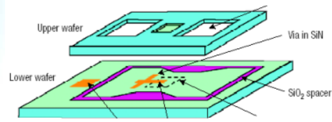
UHV



SXS/HRDFS

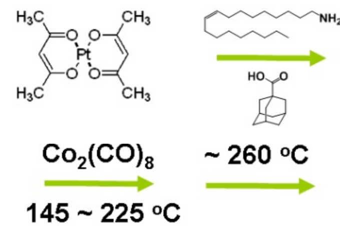


FTIR

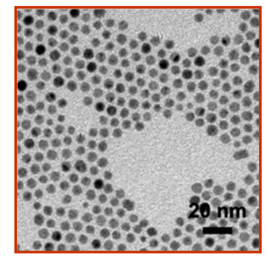


HRTEM

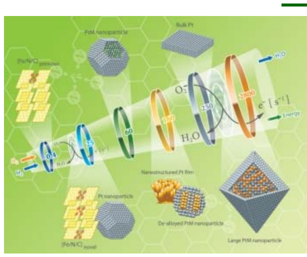
Synthesis



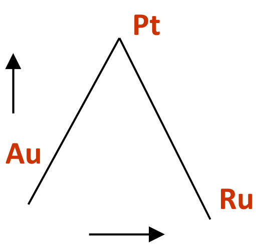
Chemical / Physical

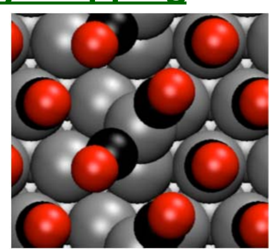


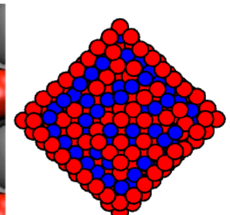
Activity and Stability Mapping



EC

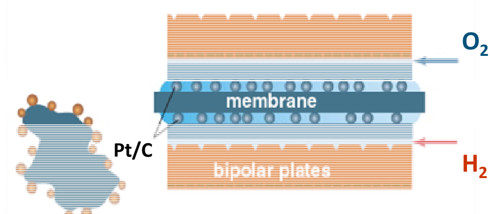






DFT/MC

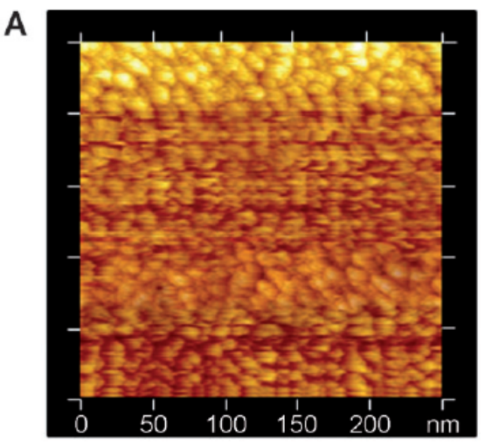
Real Applications



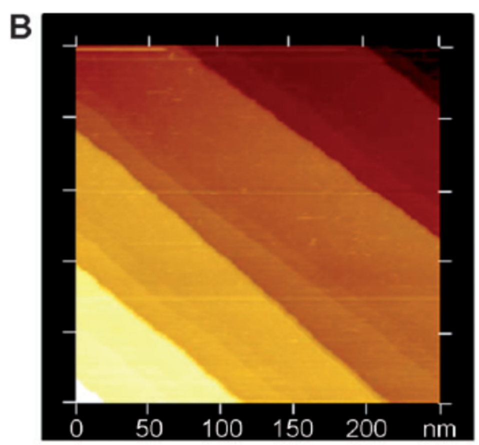
FUEL CELLS / BATTERIES / ELECTROLIZERS

Surface Structure + Composition: *Pt_3Ni[hkl] Surfaces*

STM

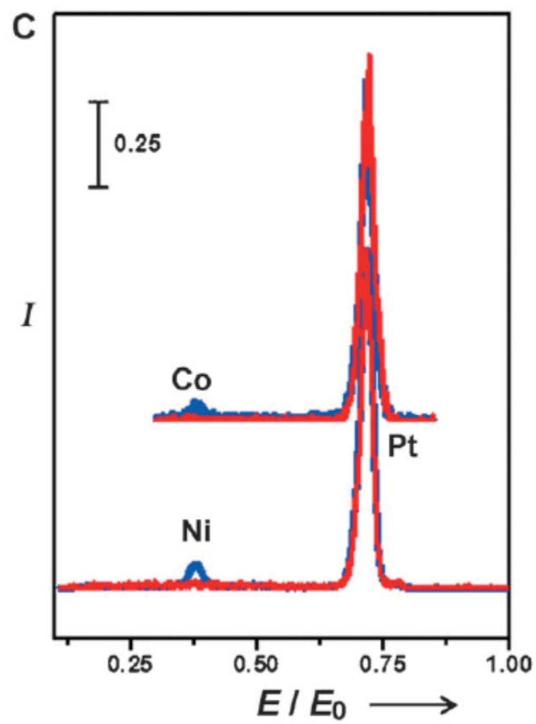


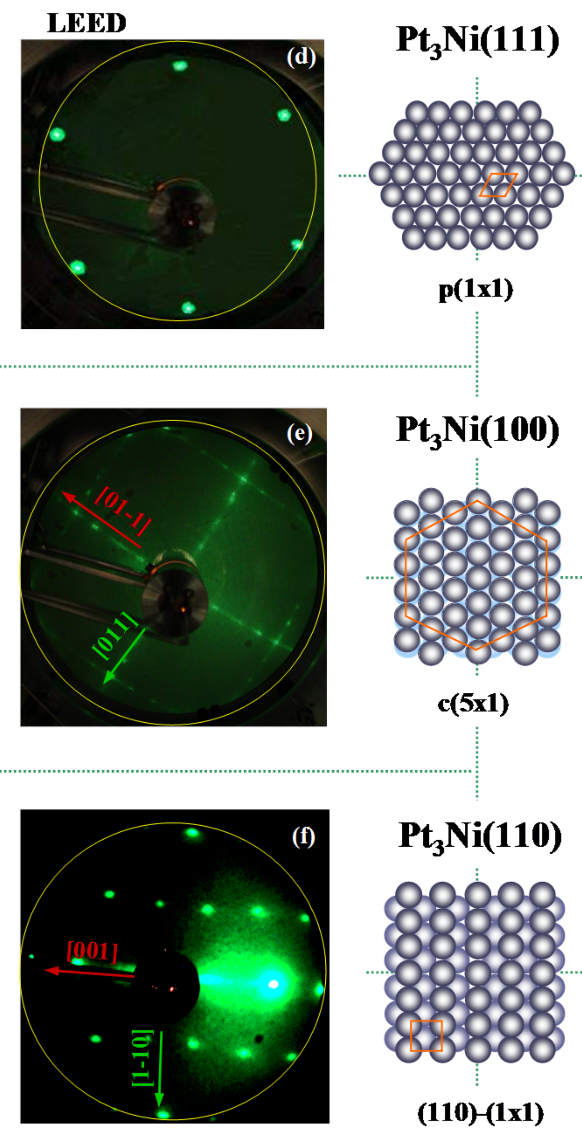
Sputtered



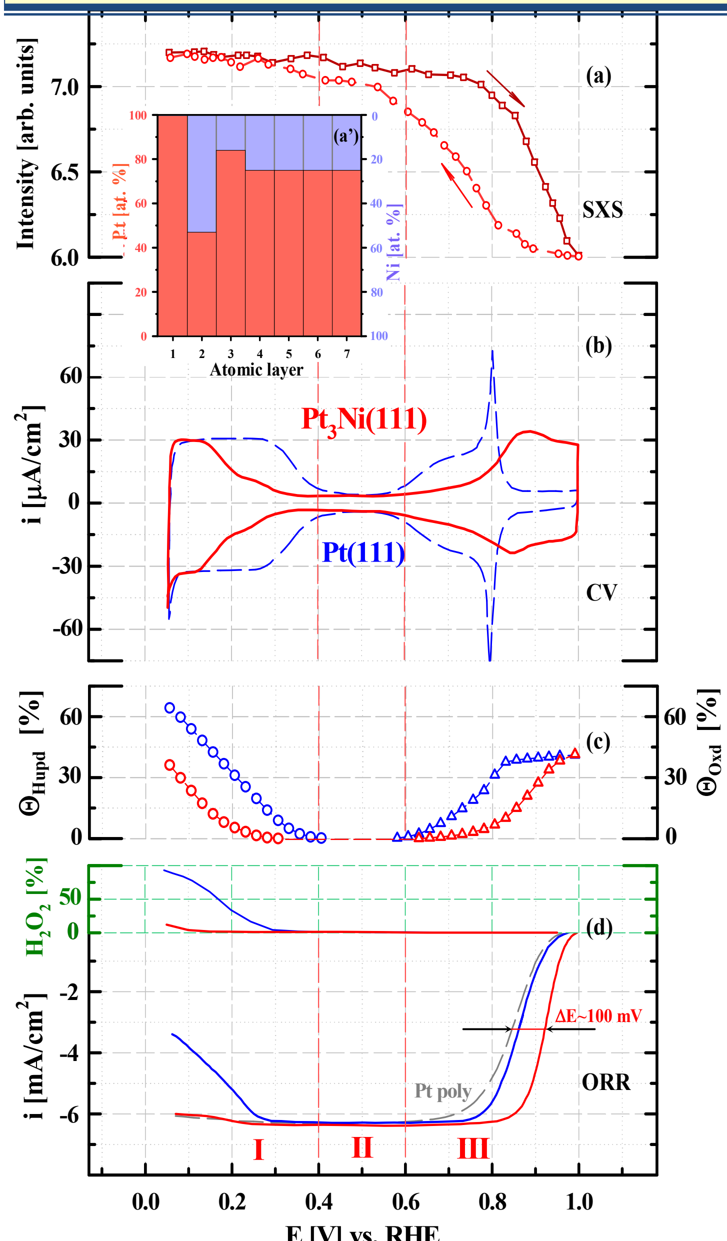
Annealed

LEIS

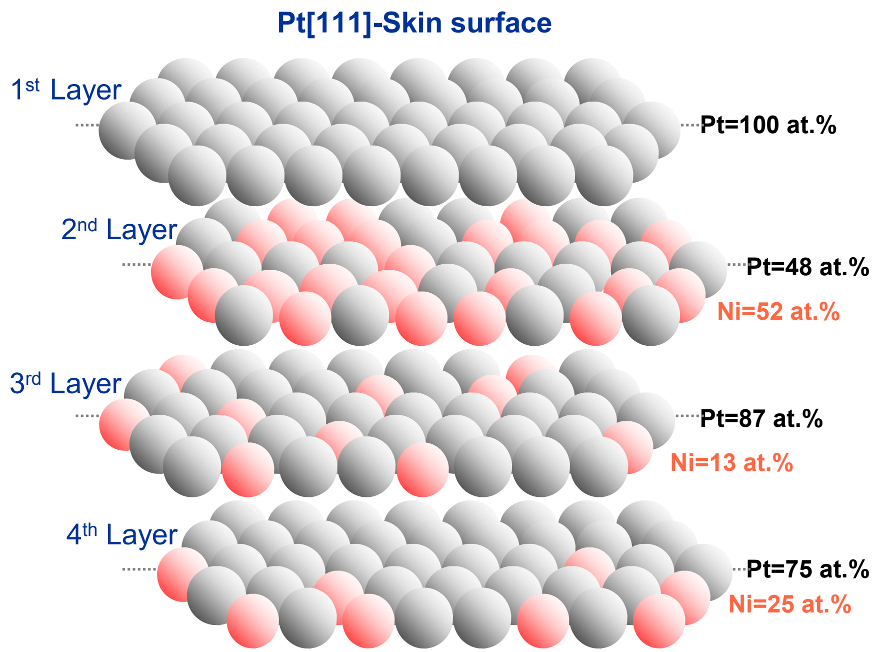




Subsurface Composition + Surface Structure: $Pt_3Ni(111)$



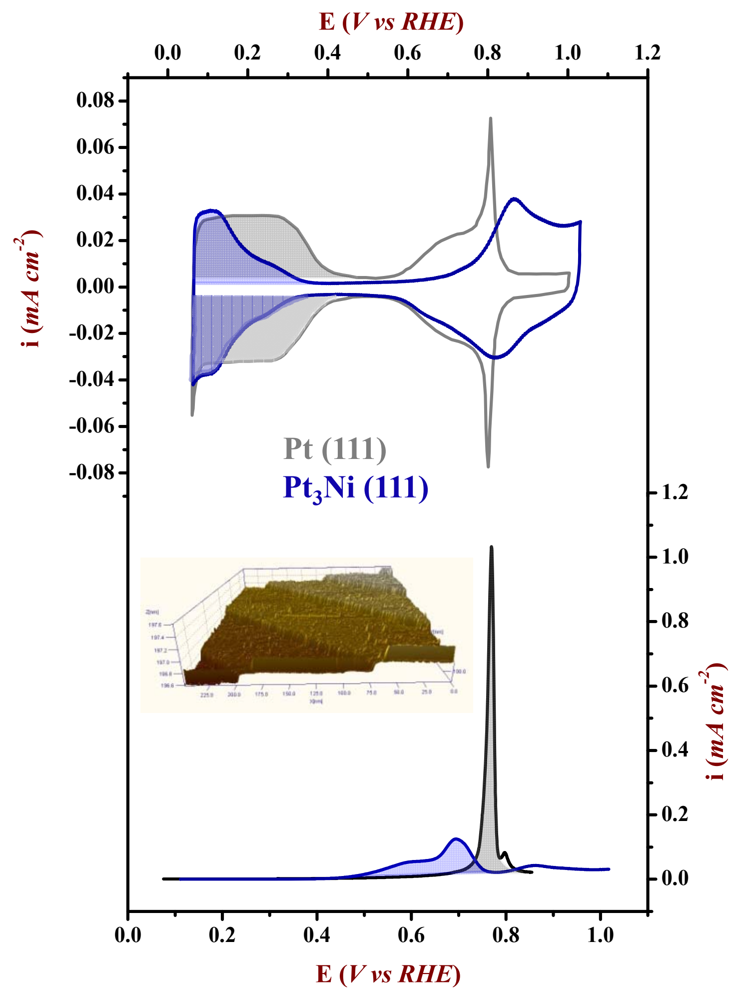
Segregation Profile



Unique Adsorption Properties of Pt-Skin Surface: *$Pt_3Ni(111)$*

Pt-skin surfaces: *Importance* to perform evaluation of electrochemically active surface area

Pt-skin surfaces on well-defined single crystal surfaces



Pt(111)-skin surfaces exhibit substantially lower coverage by H_{upd} vs. Pt(111)
(up to 50% lower H_{upd} region is obtained on Pt(111)-Skin)

Surface coverage of adsorbed CO is not affected on Pt-skin surfaces

Surface	Q_H ($\mu C/cm^2$)	Q_{CO} ($\mu C/cm^2$)	Q_{CO} / $2Q_H$
Pt (111)	152	315	1.04
Pt_3Ni (111)	98	304	1.55
Pt (poly)	190	386	1.02

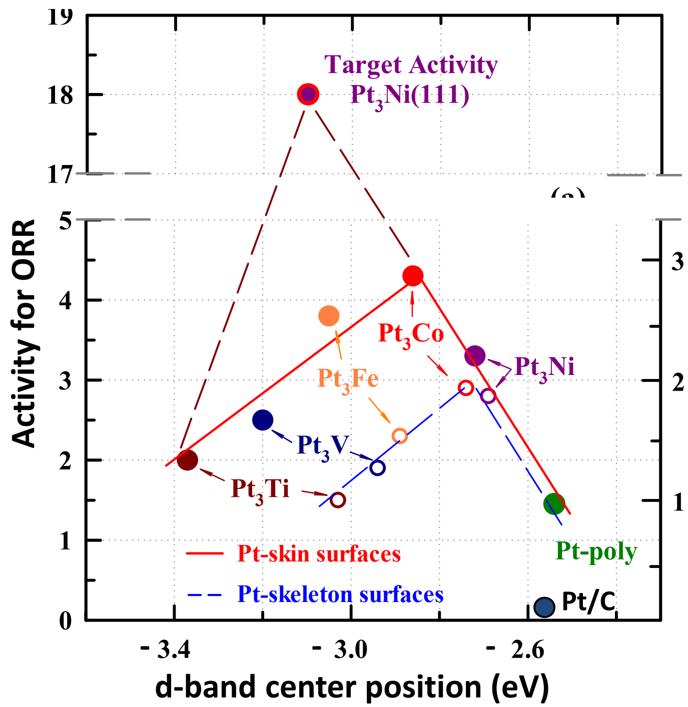
Electrooxidation of adsorbed CO (CO stripping) has to be performed for Pt-skin surfaces in order to avoid underestimation of electrochemically active surface area and overestimation of specific activity

Same effect was confirmed on Pt-skin thin film surfaces

Activity Trends for PtM Alloys: *Subsurface Composition*

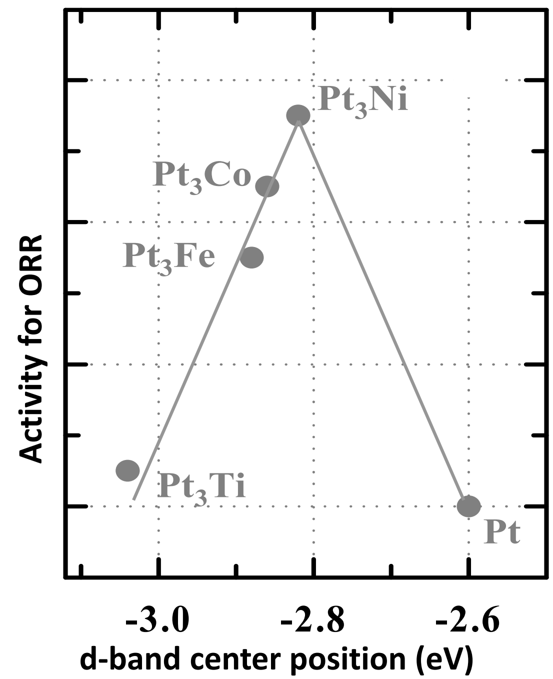
In situ characterized and computationally predicted nanosegregated structures (4-5 atomic layers) **are the most active catalysts for the ORR (~100 times more active than Pt/C catalysts)**

Experimental activity trends



Nature Materials, 6(2007)241

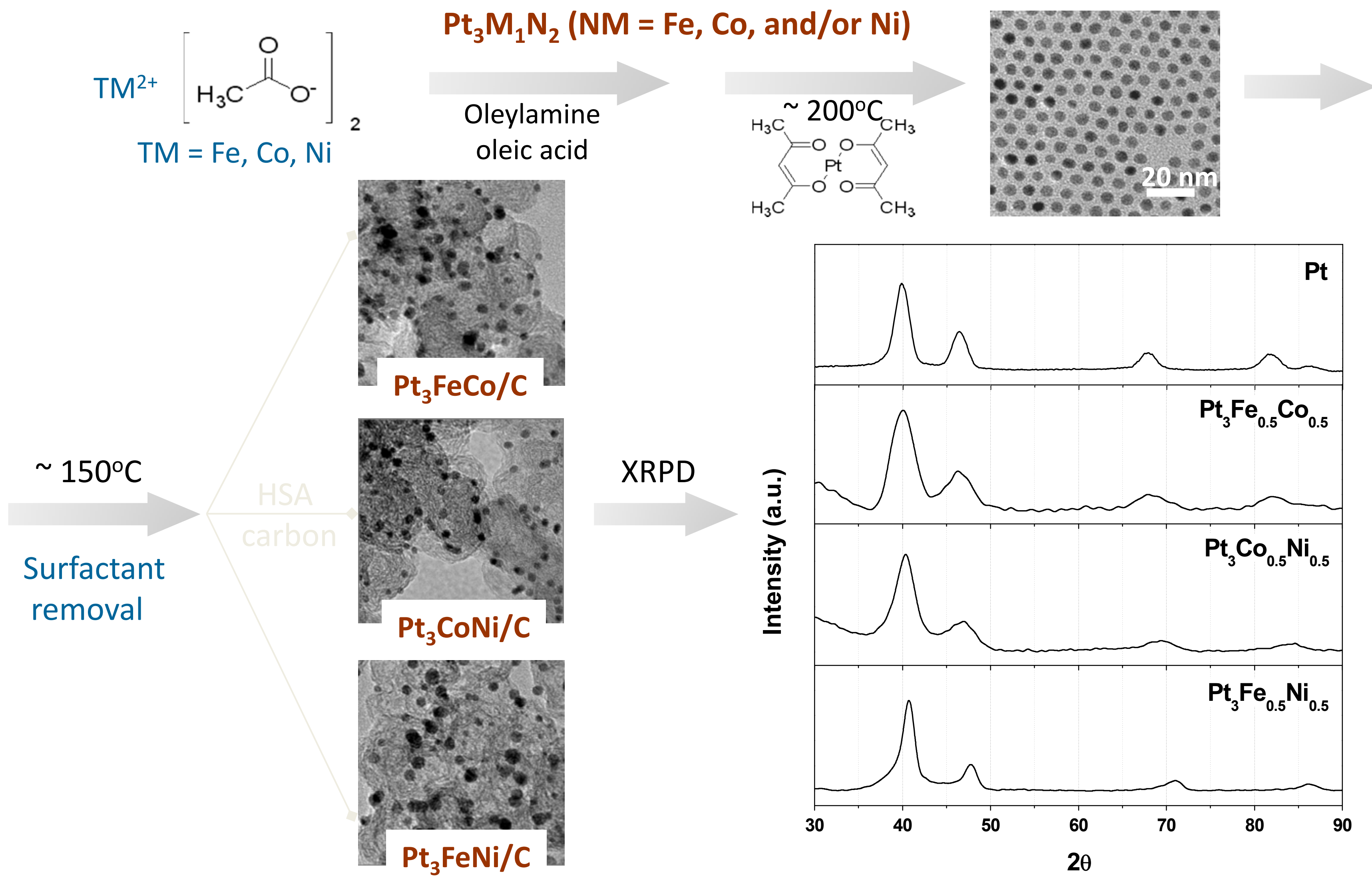
Theoretical activity tremds



Angew. Chem. Int. Ed, 45(2006)2897

Electrocatalytic activity does not originate only from surface atoms

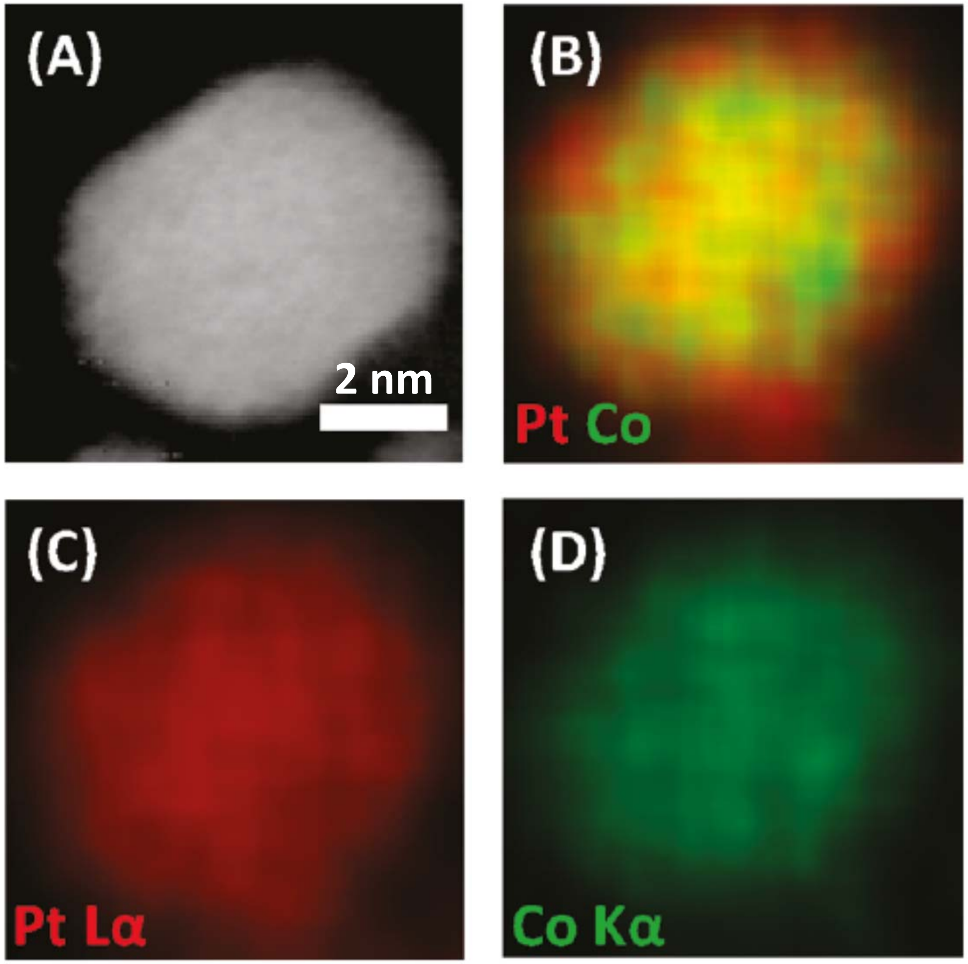
SYNTHESIS: Colloidal solvo - thermal approach has been developed for monodispersed binary and ternary PtM and PtMN nanoparticles with controlled size and composition



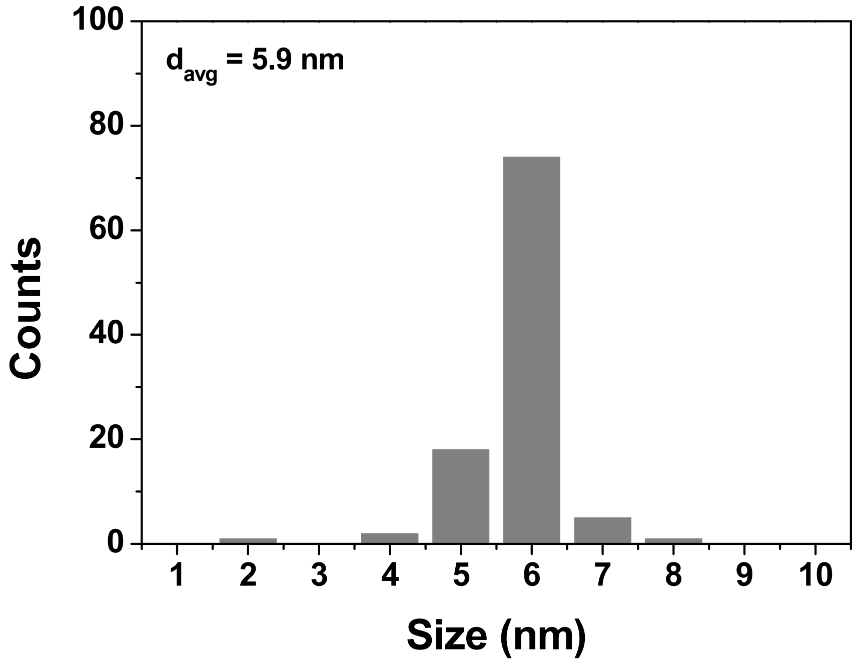
Efficient surfactant removal method does not change the catalyst properties

Pt_3Co Alloy NPs | Distribution: *Elements and Particle Size*

HAADF - STEM

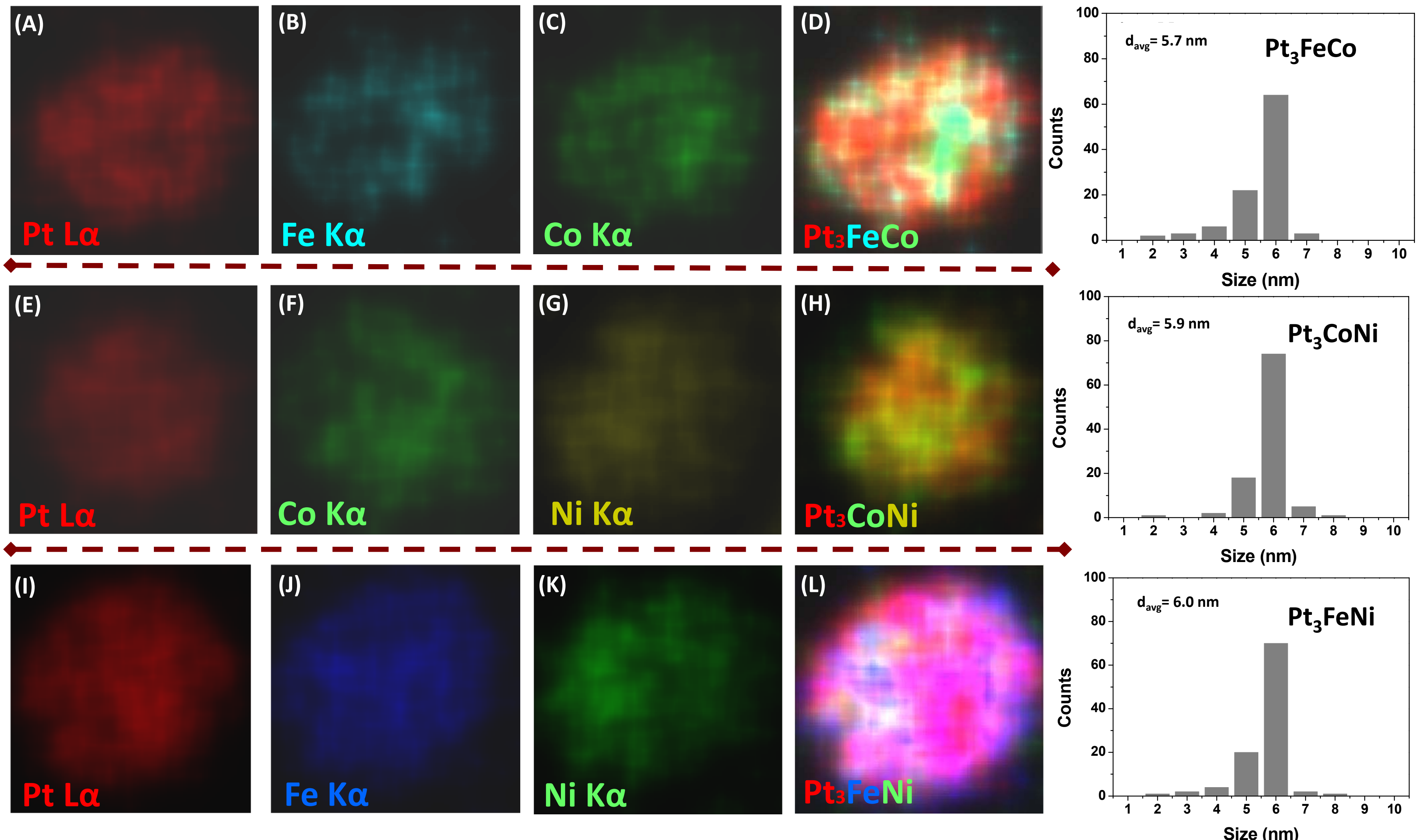


Particle size distribution



Pt_3MN Alloy NPs | Distribution: *Elements and Particle Size*

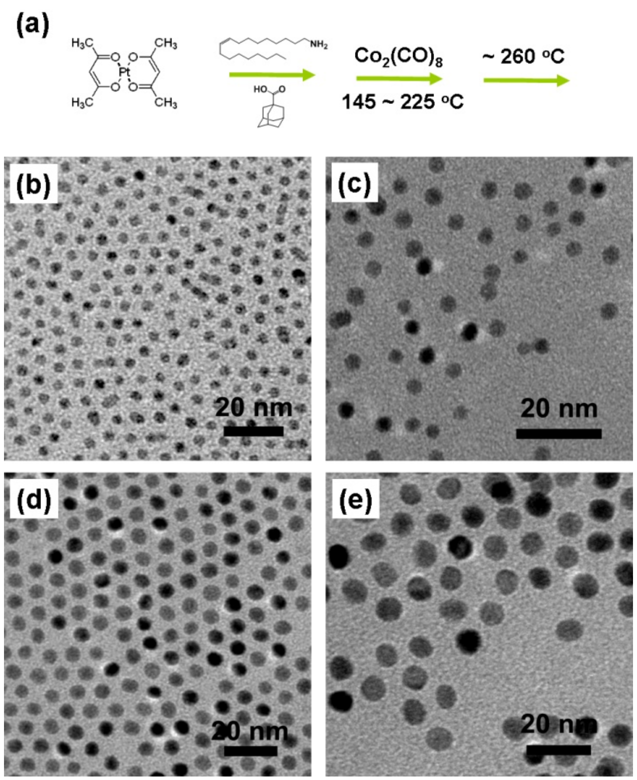
EDS/STEM: *Elemental mapping and particle size distribution*



Highly homogeneous and monodisperse ternary alloy nanoparticles

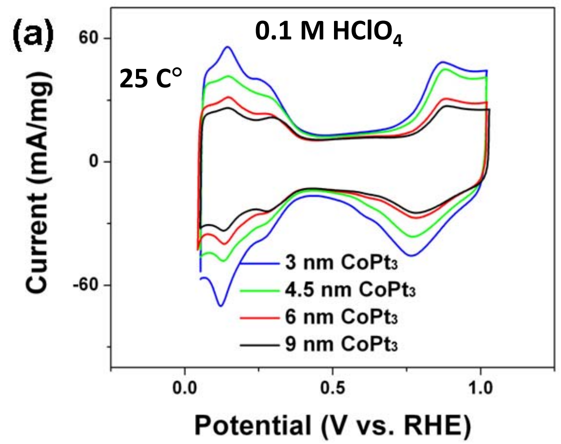
Particle Size Effect: *Pt-Alloy NPs*

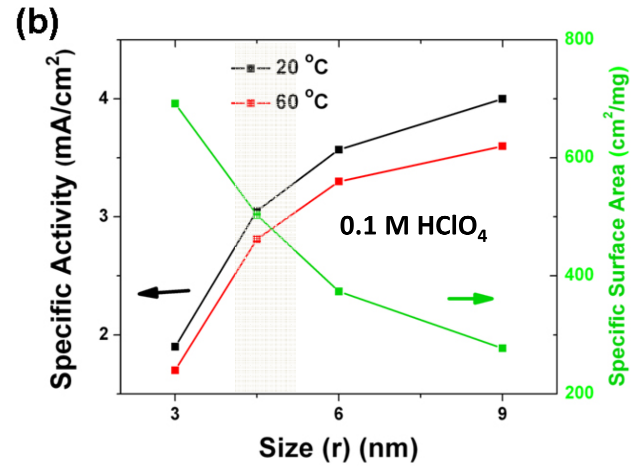
Colloidal deposition approach is used to synthesize (a) monodispersed Pt_3Co bimetallic NPs with diameter of 3, 4.5, 6 and 9nm

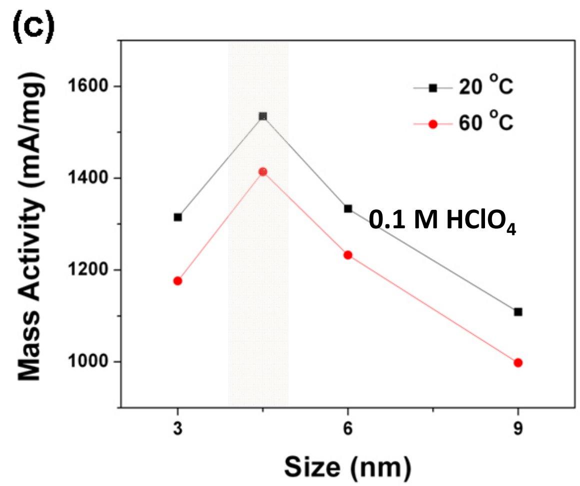


Particle size is determined by analyzing TEM images (b-e)

Particle size effect applies to Pt-Alloy NPs





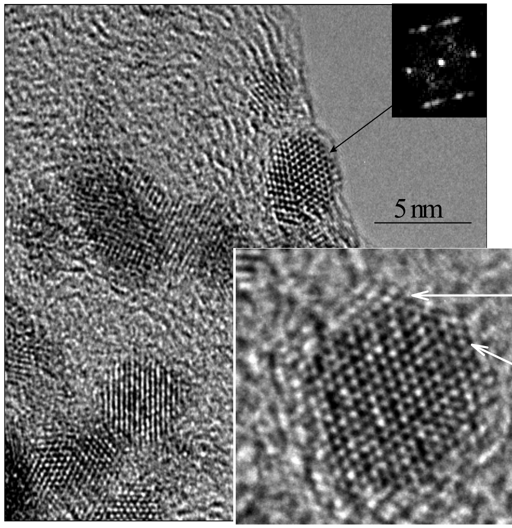


Specific surface area is determined from Θ_{Hupd}

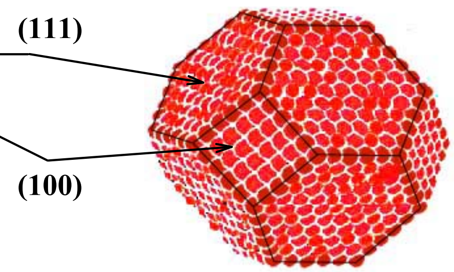
Specific Activity increases with particle size: 3 < 4.5 < 6 < 9nm

Mass Activity decreases with particle size: optimal size ~5nm

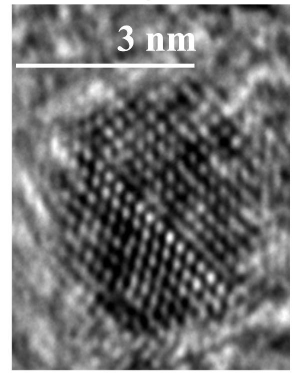
Pt based NPs: *Particle Size Effect*



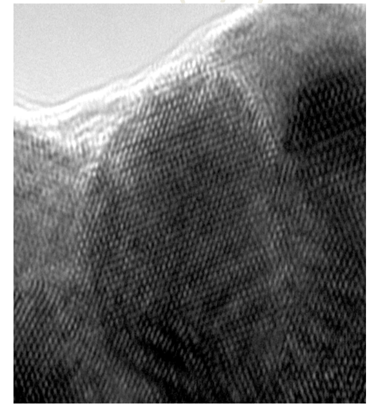
❑ cubo-octahedral particles



10 % Pt/Vulcan

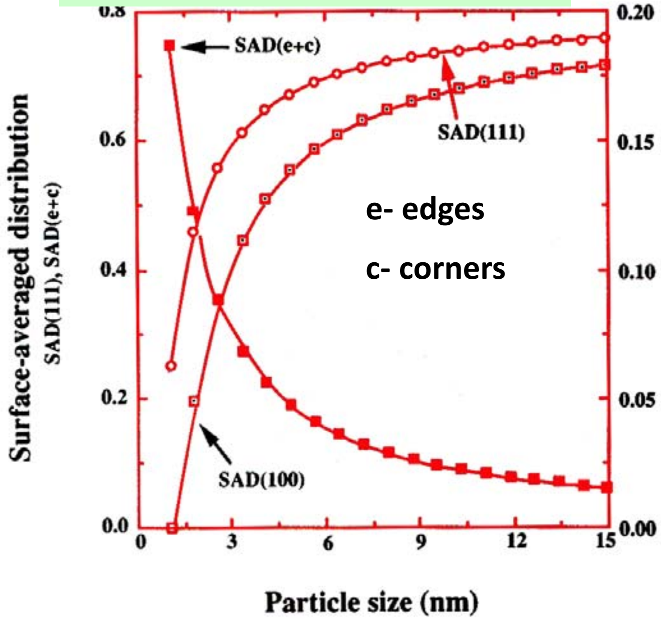


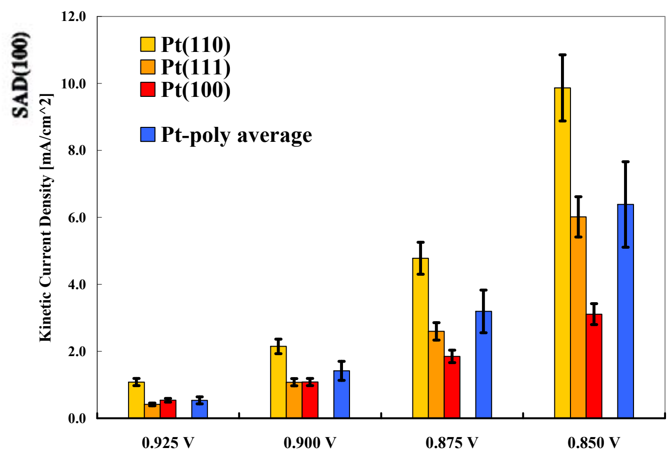
30 nm (Pt/C)



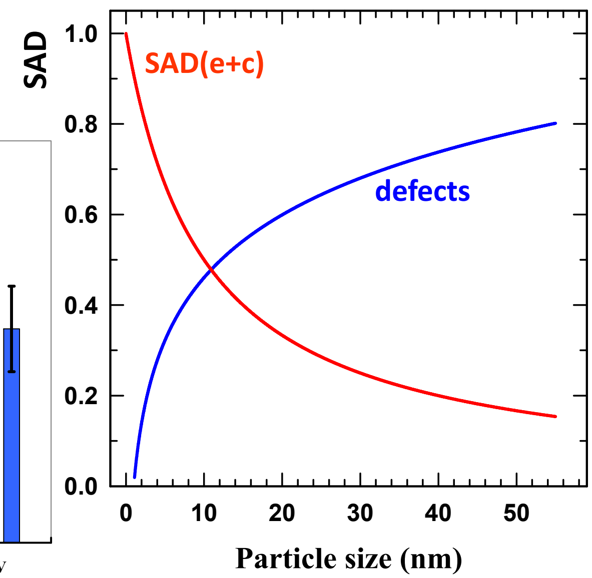
❑ "Real" particles

❑ "Ideal" particles

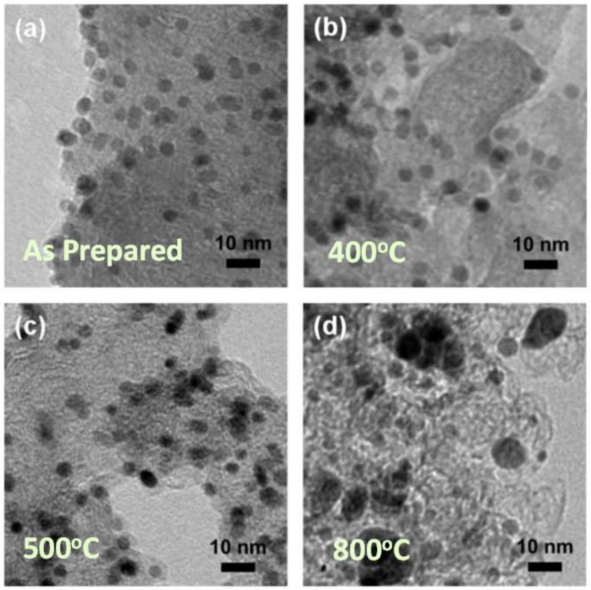




Rough particles: steps, "rounded" planes, twins, grain boundaries, irregular facets

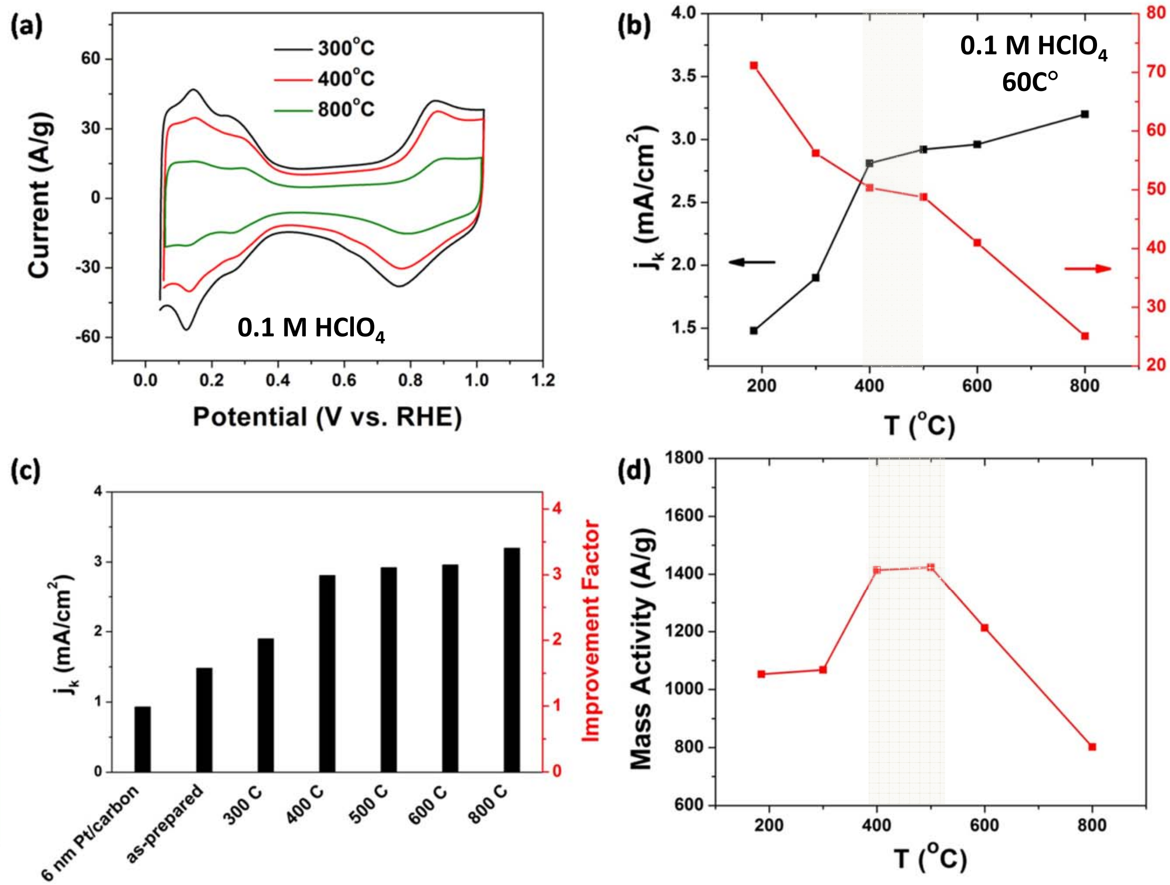


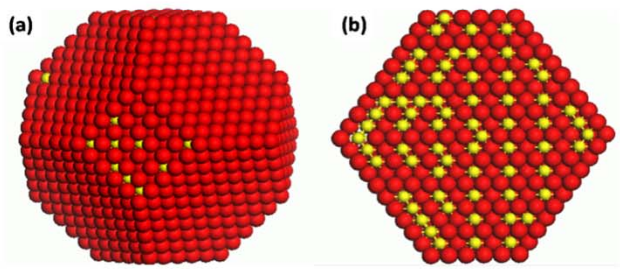
Pt Alloy NPs: *Annealing*



TEM: no agglomeration below 500°C

Temperature Induced Segregation: apply 400 to 500°C to optimize catalytic activity of the ORR on PtCo bimetallic NPs





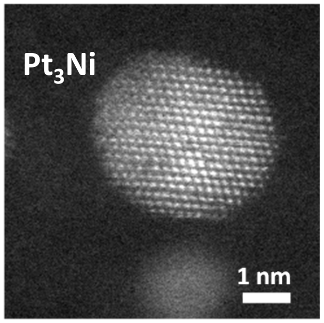
External View   Cross Section

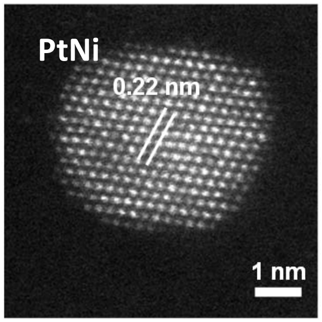
MC simulations at 400°C confirmed segregation profile of Pt_3Co NPs, which was experimentally observed for extended surfaces

Annealing above 500°C provides small increase in specific activity but significant decrease in mass activity of Pt_3Co NPs

Pt Alloy NPs: *Composition and Surface Chemistry*

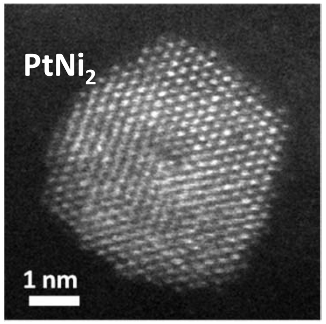
Colloidal method is used to synthesize Pt_xNi_{1-x} NPs with 3:1, 1:1, 1:2 and 1:3 atomic ratio

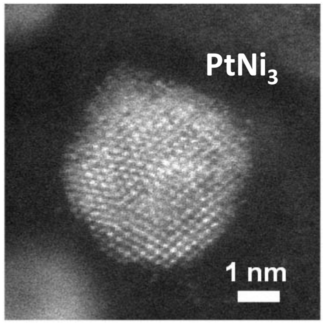


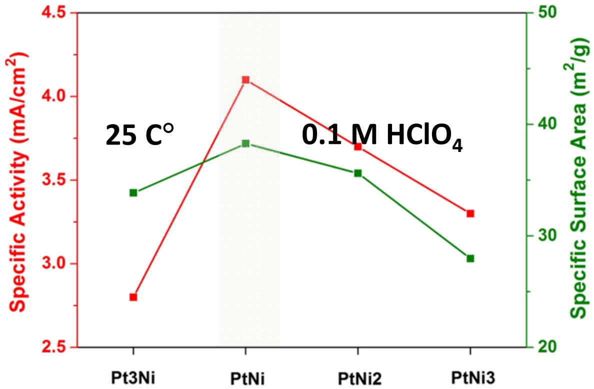


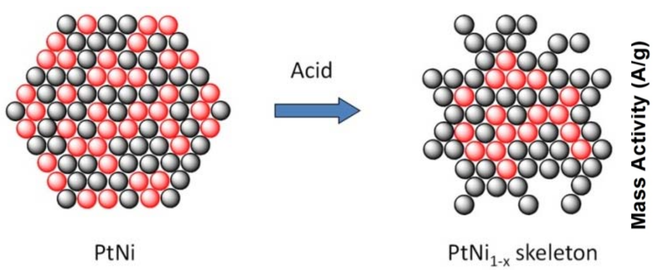
~5nm Pt_xN_{1-x}

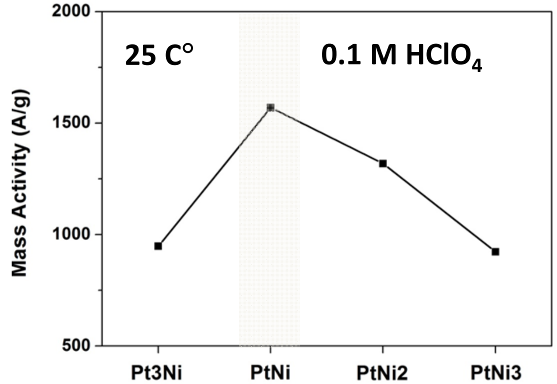
Last step annealing at 400°C











Maximum activity obtained for as-synthetized NPs with 1:1 Pt to Ni atomic ratio

In acidic environment, atomic % of Ni in Pt_xNi_{1-x} NPs decreases due to dissolution of Ni surface atoms

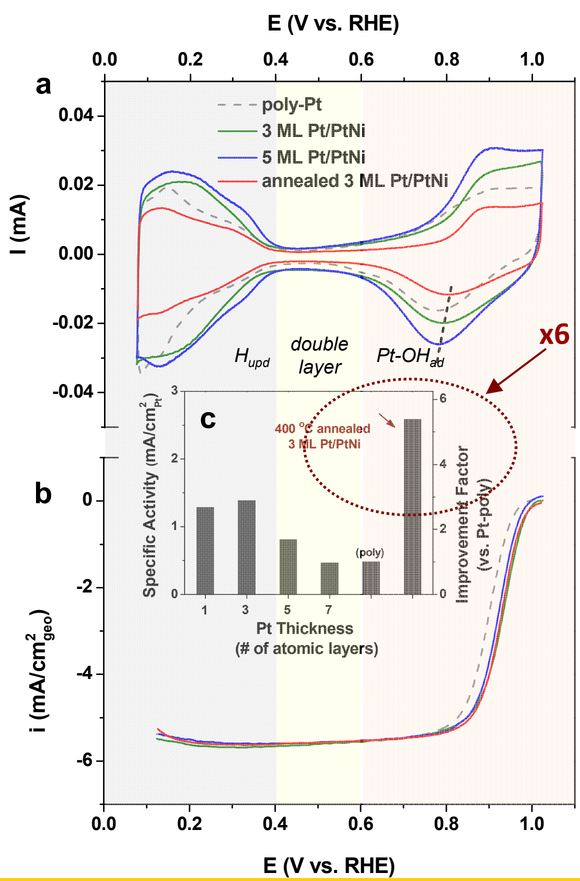
Pt_3Ni ➡ $Pt_{85}Ni_{15}$ PtNi ➡ $Pt_{75}Ni_{25}$ $PtNi_2$ ➡ $Pt_{80}Ni_{20}$ $PtNi_3$ ➡ $Pt_{90}Ni_{10}$

PtNi transforms into Pt_3Ni skeleton

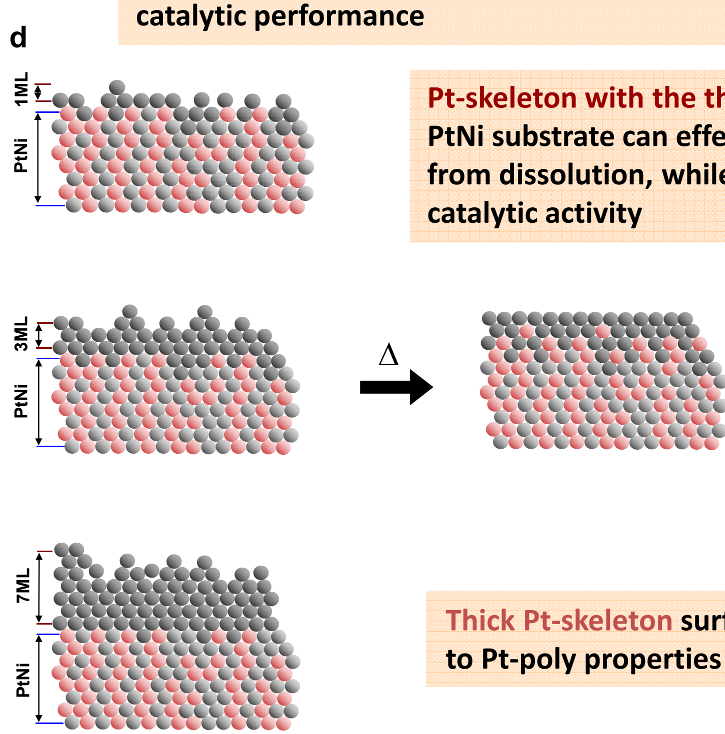
Segregation of Pt at 400°C is not complete in Pt_xNi_y NPs, which induces dissolution of Ni

Surface Optimization: *Pt-skeleton thickness*

Thin Pt bi/multi metallic film studies: Physical vapor deposition over the substrates with adjustable compositions



Pt-skeleton thickness has direct influence on catalytic performance

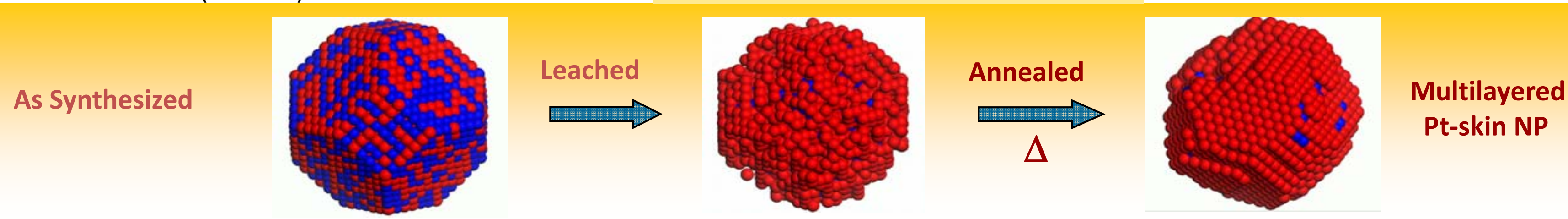


Pt-skeleton with the thickness of 3ML above PtNi substrate can effectively protect Ni from dissolution, while maintaining high catalytic activity

Annealed Pt-skeleton surface forms multilayered skin type of surface with superior catalytic properties (x6 vs. Pt-poly)

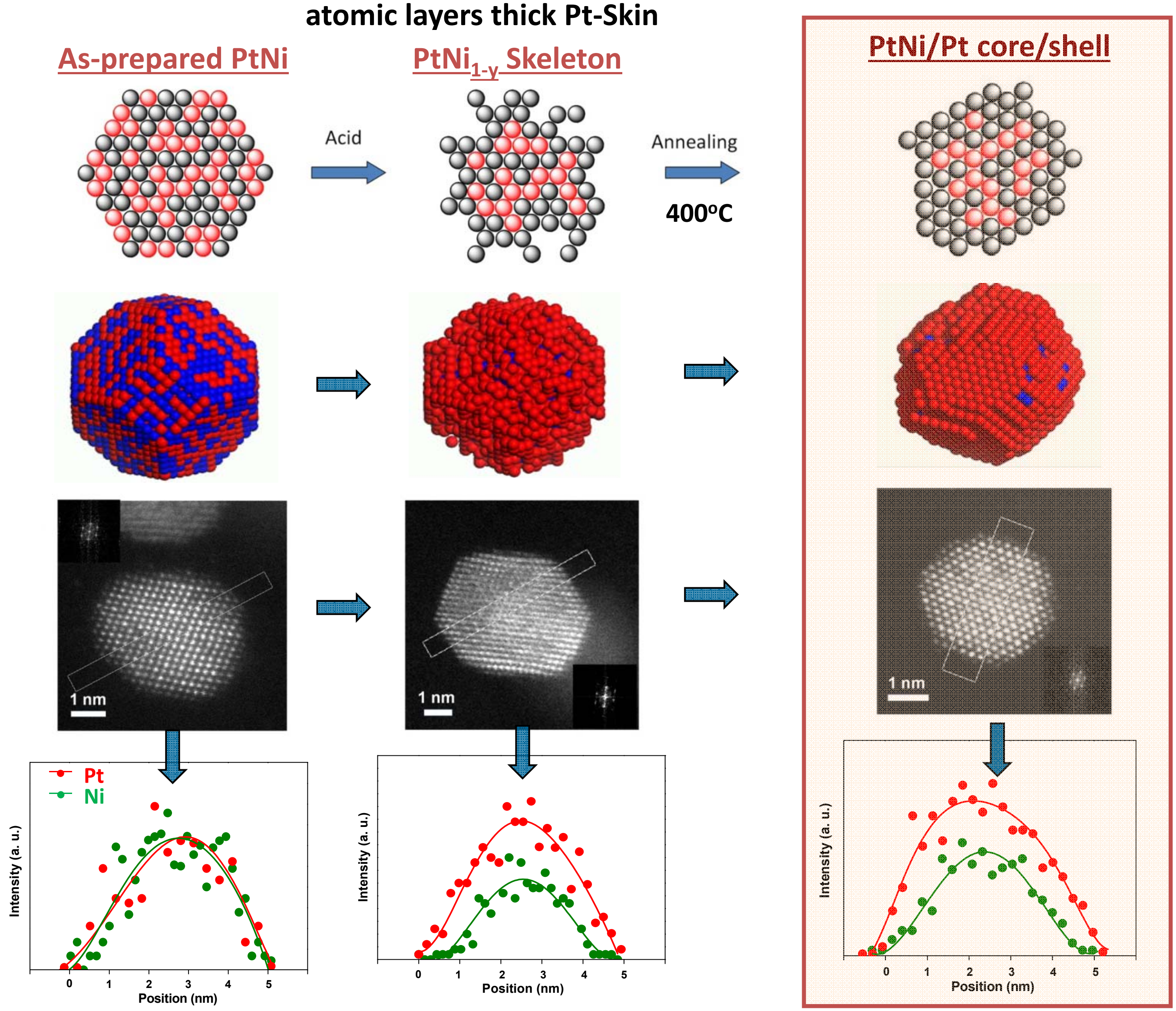
Thick Pt-skeleton surfaces converge to Pt-poly properties

Transfer to nanoscale systems



PtNi: *Tailoring the Structure at Nanoscale*

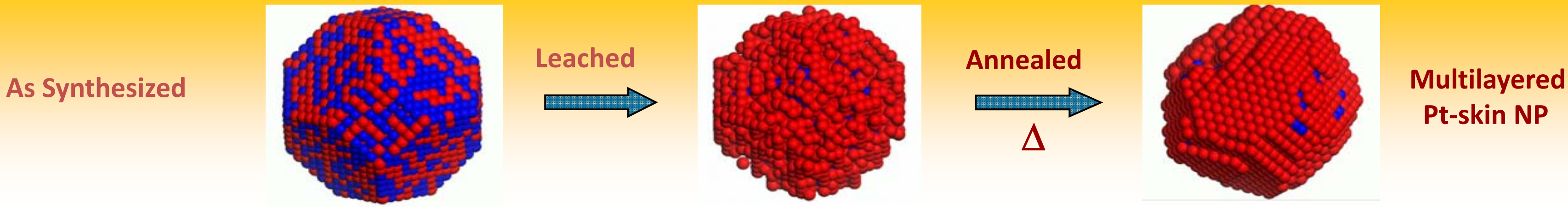
Temperature annealing protocol used to transform $PtNi_{1-x}$ skeletons to multilayered PtNi/Pt NPs with 2-3 atomic layers thick Pt-Skin

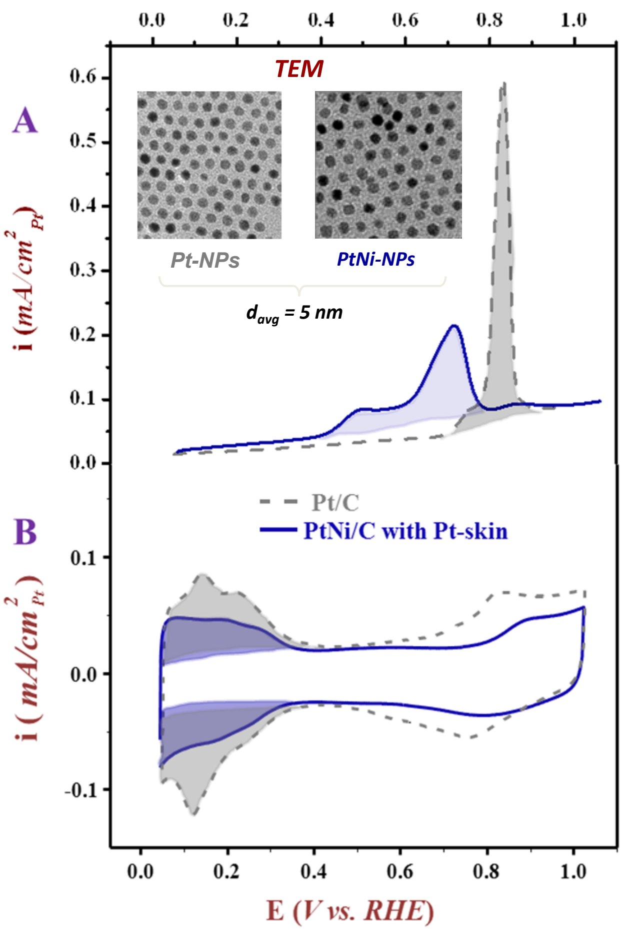


HRTEM

Line profile

Unique Adsorption Properties of Pt-Skin Surface: *PtNi/C*





Catalysts with multilayered Pt-skin surfaces exhibit substantially lower coverage by H_{upd} vs. Pt/C
(up to 40% lower H_{upd} region is obtained on Pt-Skin catalyst)

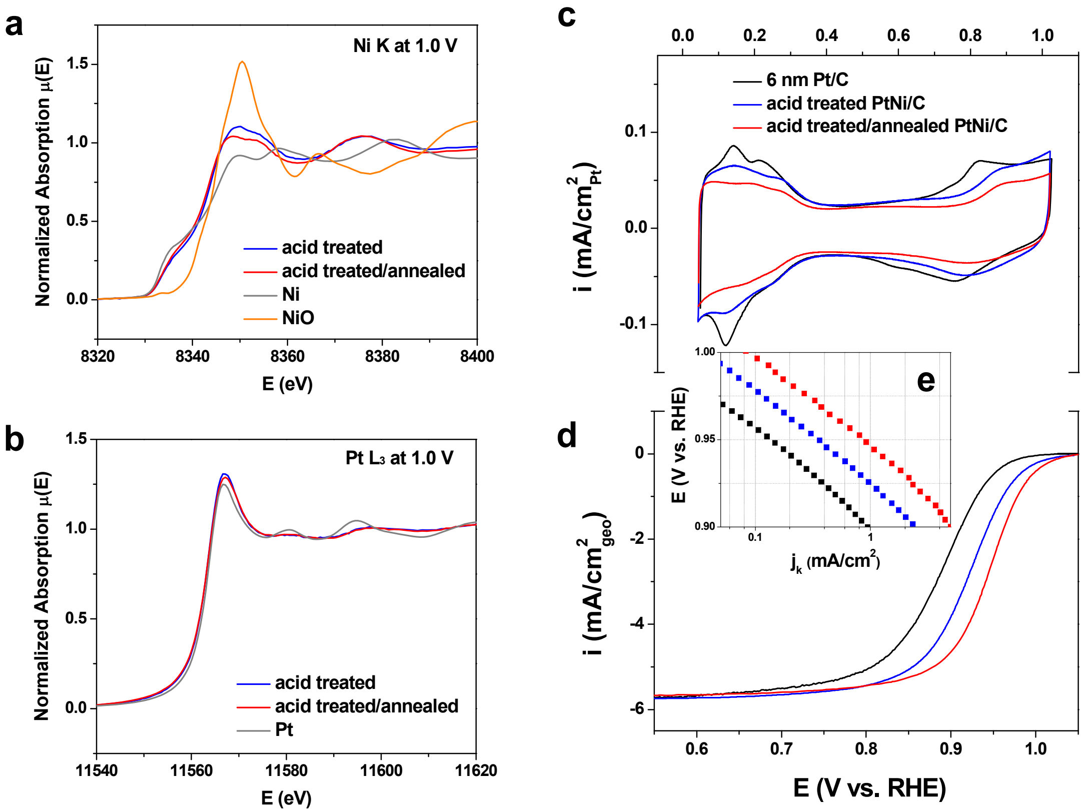
Surface coverage of adsorbed CO is not affected on Pt-skin surfaces

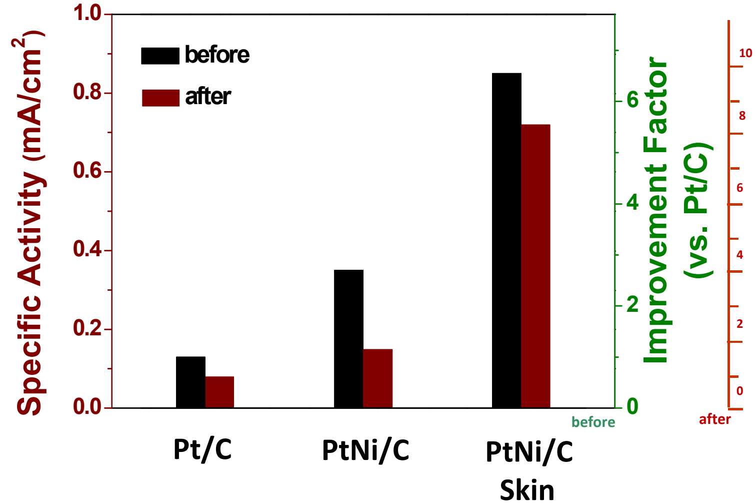
Ratio of Q_{CO}/Q_{Hupd}>1 is indication of Pt-skin formation

Catalyst	Q_H (μC)	$ECSA_H$ (cm²)	Q_{CO} (μC)	$ECSA_{CO}$ (cm²)	$Q_{CO}/2Q_H$
Pt/C	279	1.47	545	1.41	0.98
PtNi/C	292	1.54	615	1.60	1.05
PtNi-skin/C	210	1.10	595	1.54	1.42

Electrooxidation of adsorbed CO **(CO stripping) has to be performed for Pt-alloy catalysts in order to avoid underestimation electrochemically active surface area and overestimation of specific and mass activities**

PtNi Catalyst: *RDE Studies of Multilayered Pt-Skin Surfaces*





20K Cycles: 0.6-1.1V

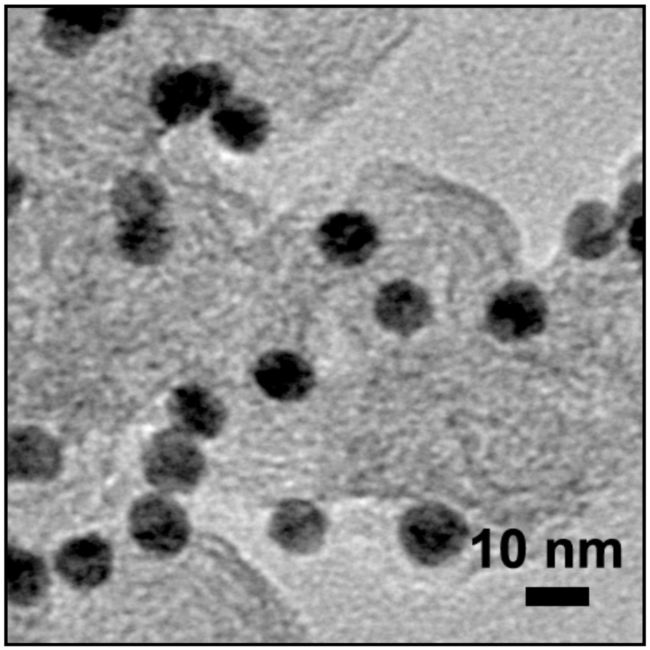
TEM/XRD: Content of Ni is maximized and allows formation of the multilayered Pt-skin by leaching/annealing

RDE: PtNi-Skin catalyst exhibits superior catalytic performance for the ORR and is highly durable system

***In-Situ* XANES:** Subsurface Ni is well protected by less oxophilic multilayered Pt-skin during potential cycling

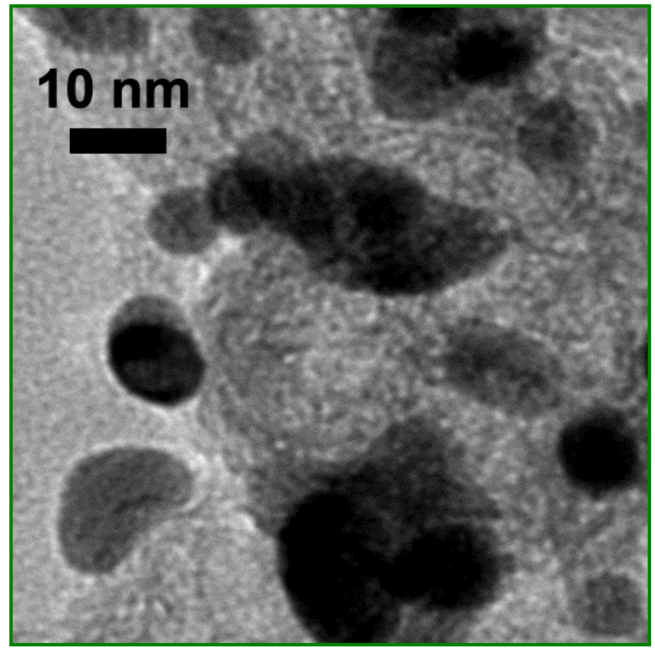
Durability: Surface area loss about 10%, SA 8 fold increase and MA 10 fold increase over Pt/C after 20K cycles

STABILITY: *Pt/C*



Pt/C

Initial morphology

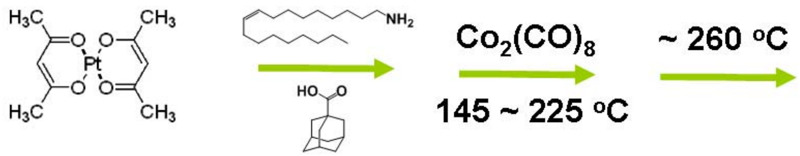


Pt/C

After 60,000 cycles

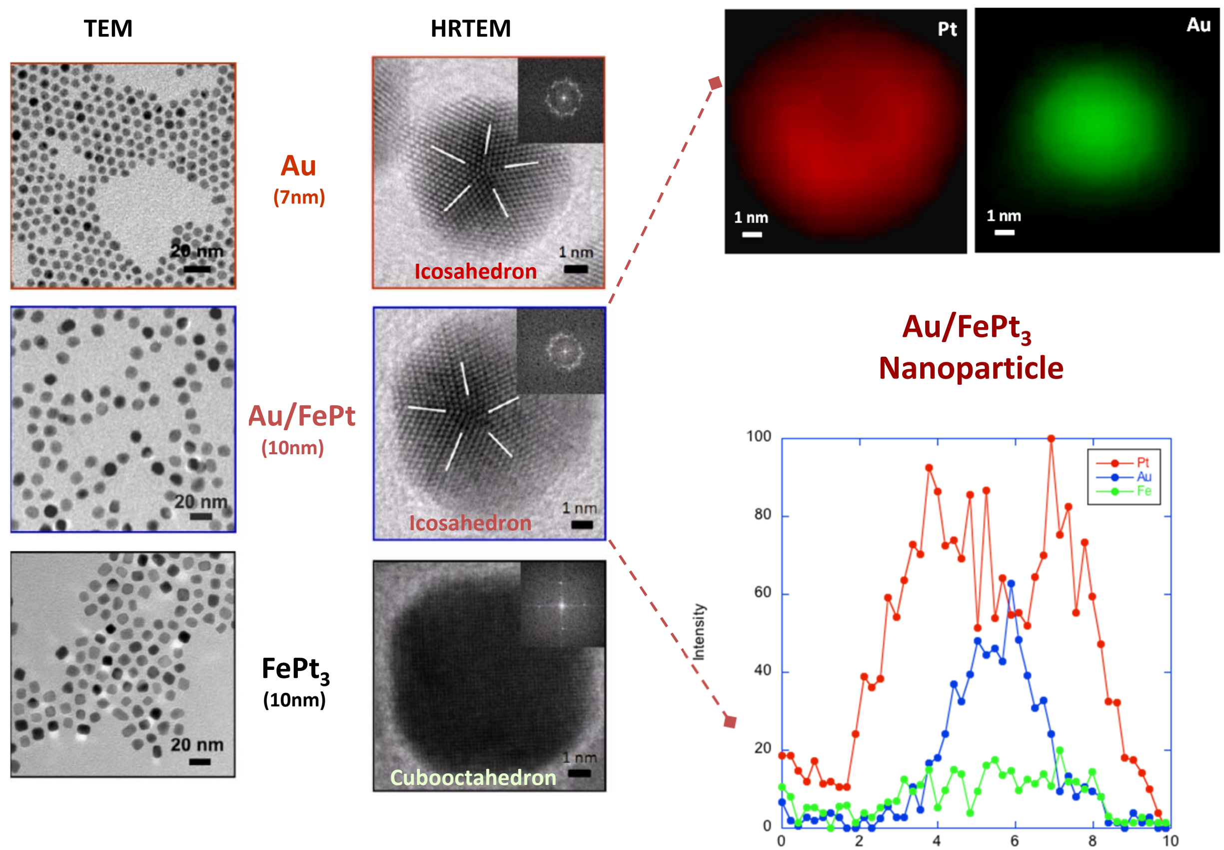
Cycle: 0.6-1.1V

STABILITY: *Pt/C, PtFe/C and Au/FePt/C*



Shape Controlled Core/Shell Particles $Au/FePt_3$

Icosahedral Au core (7nm) is synthesized chemically and coated with 1.5nm Pt-bimetallic shell



$Au/FePt_3$: *Durability Studies*

Initial morphology

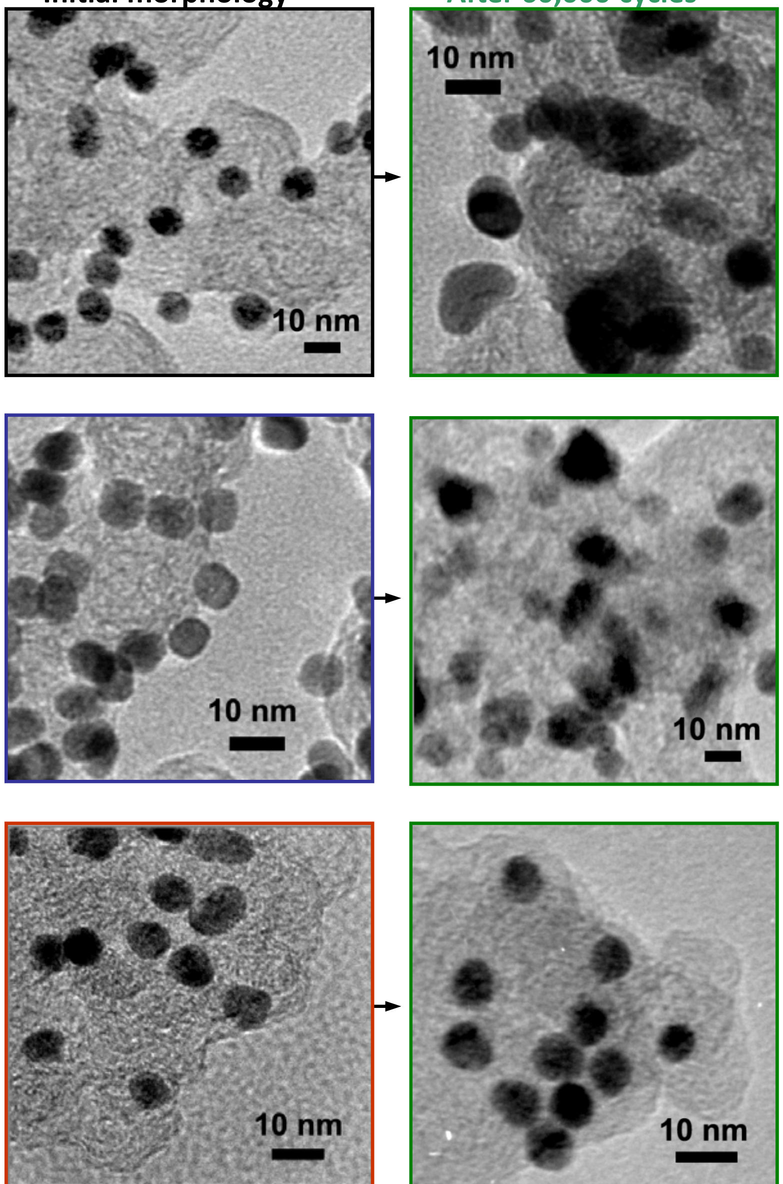
After 60,000 cycles

Pt/C

$FePt_3/C$

$Au/FePt_3/C$

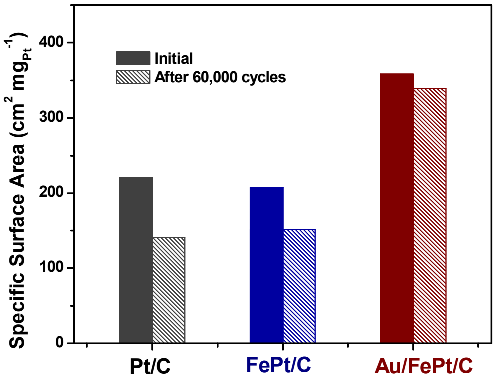
Highly Stable Electrocatalyst



$Au/FePt_3/C$

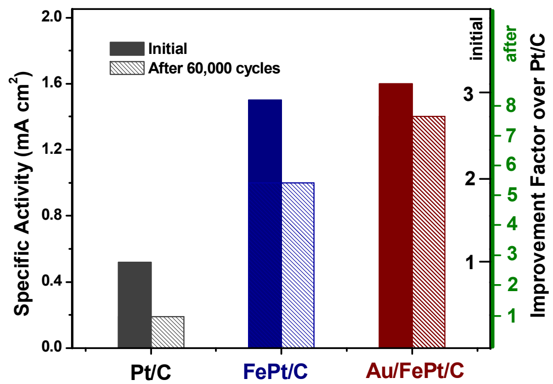
Surface Area Loss

<10%



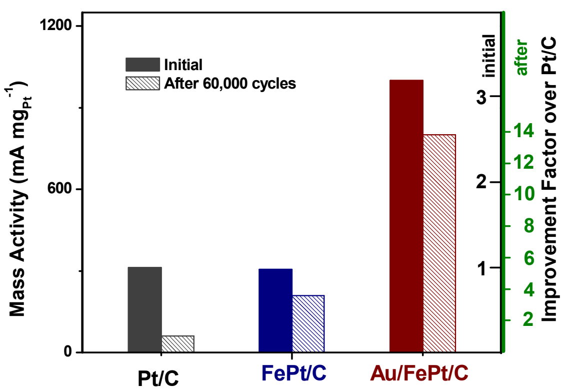
Spec. Activity

>7 times

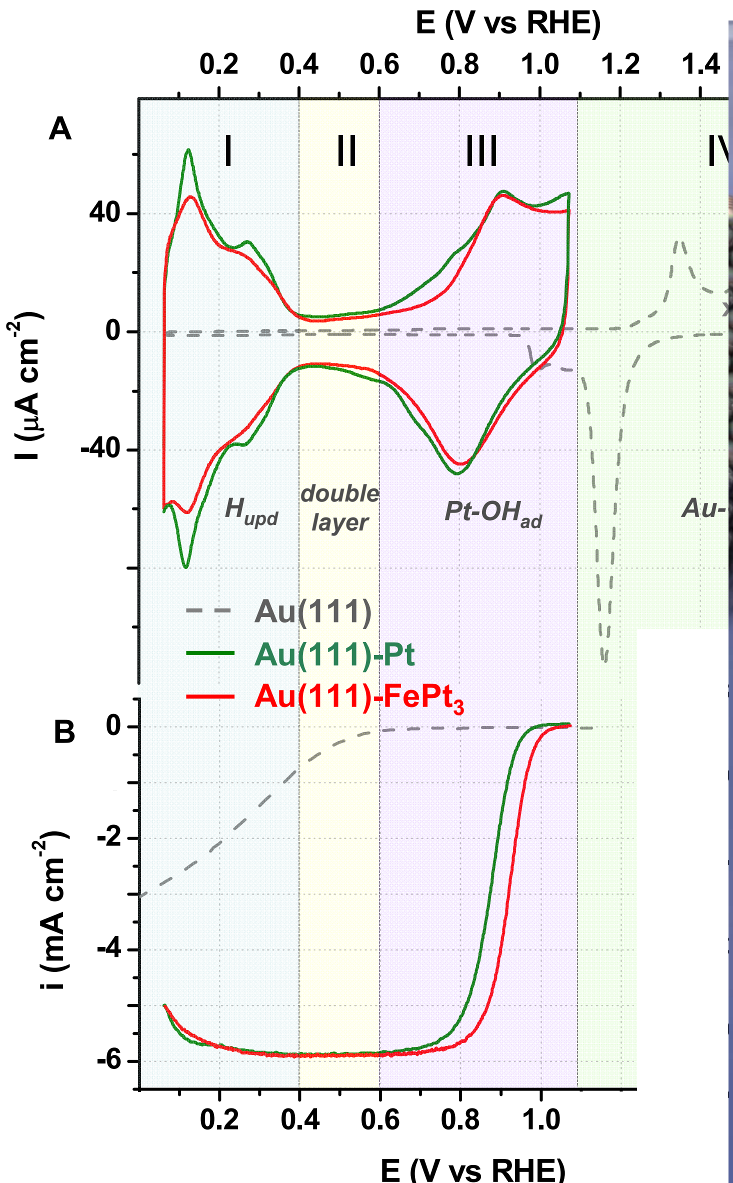


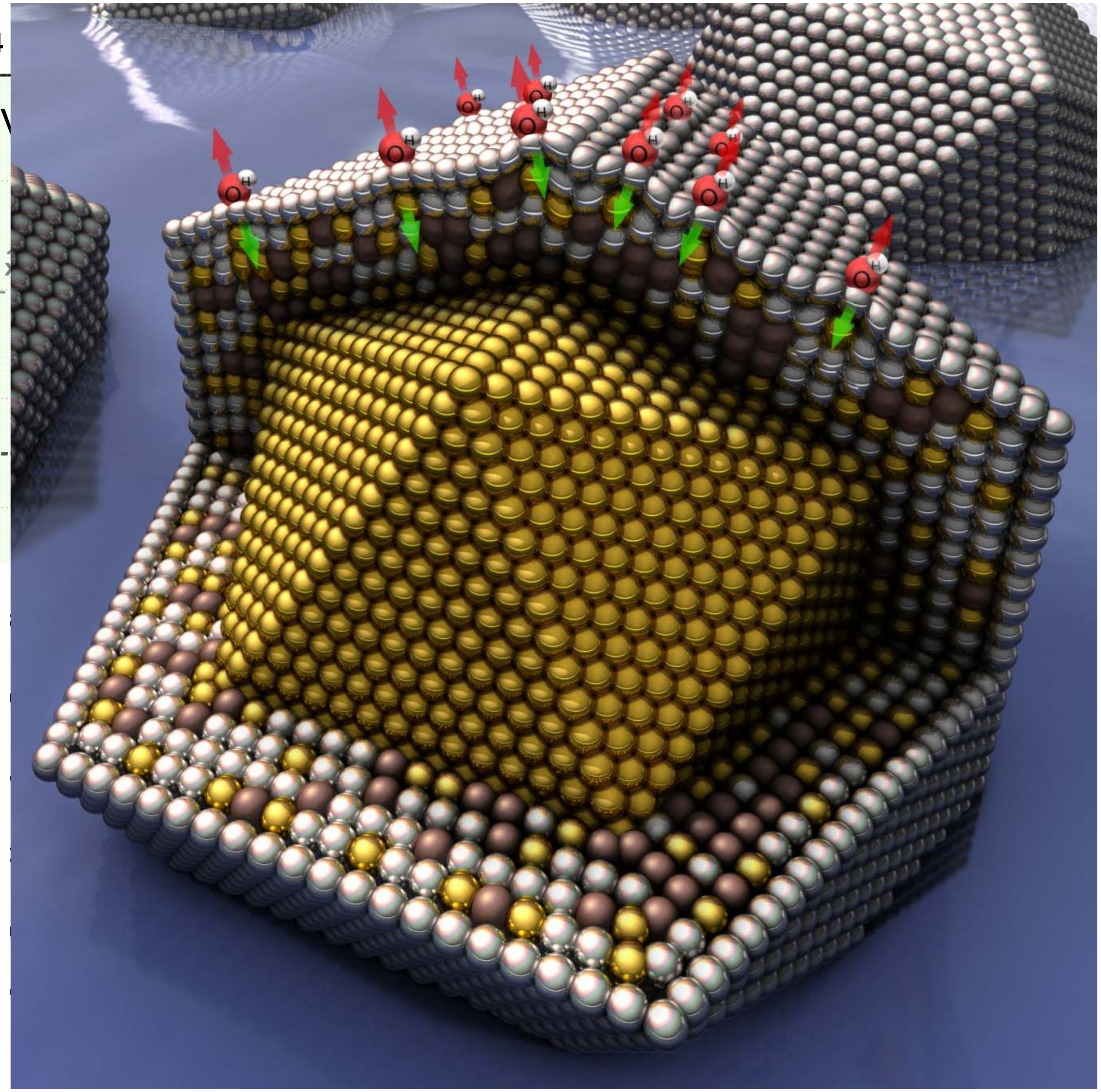
Mass. Activity

>10 times

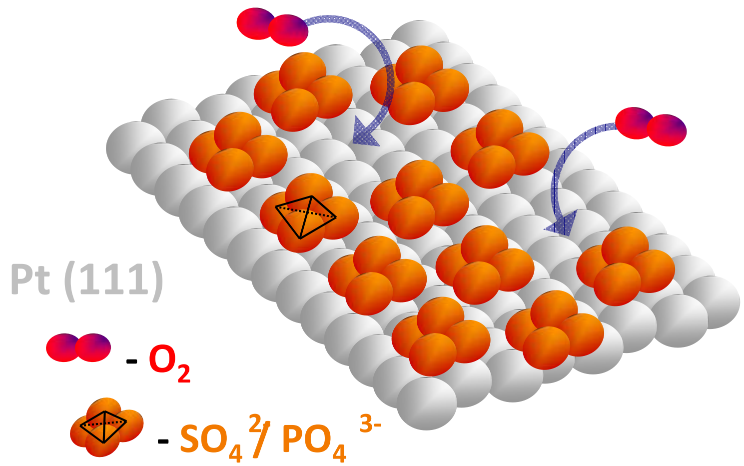


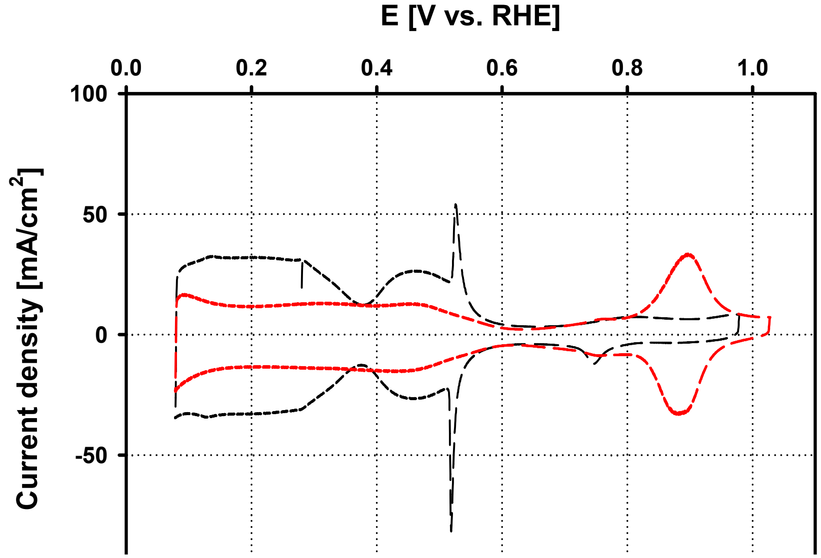
STABILITY: *Mechanism of Improvement*



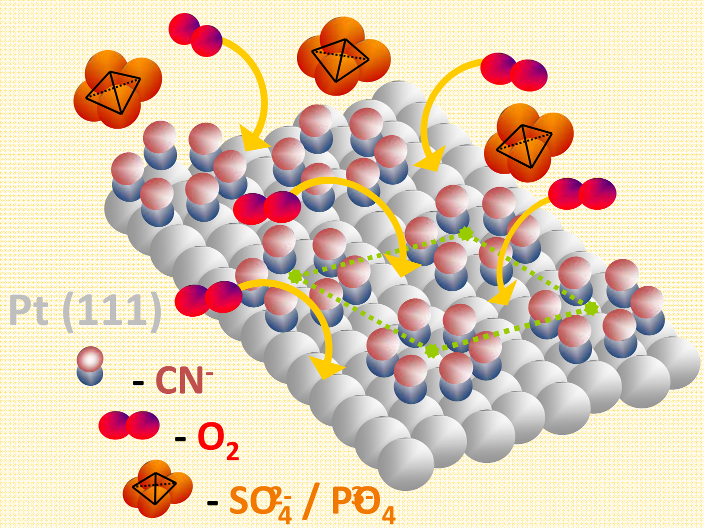


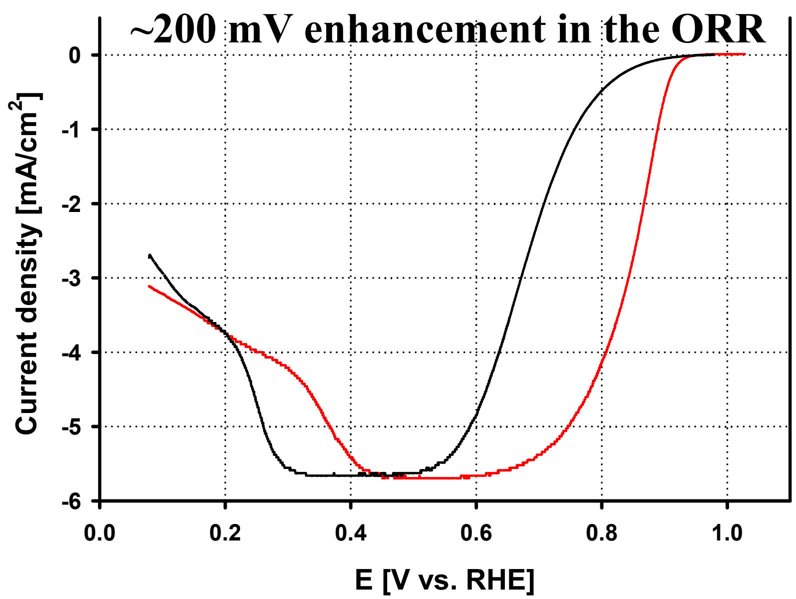
SELF ASSEMBLED ADLAYERS: *Pt(111)-CN*





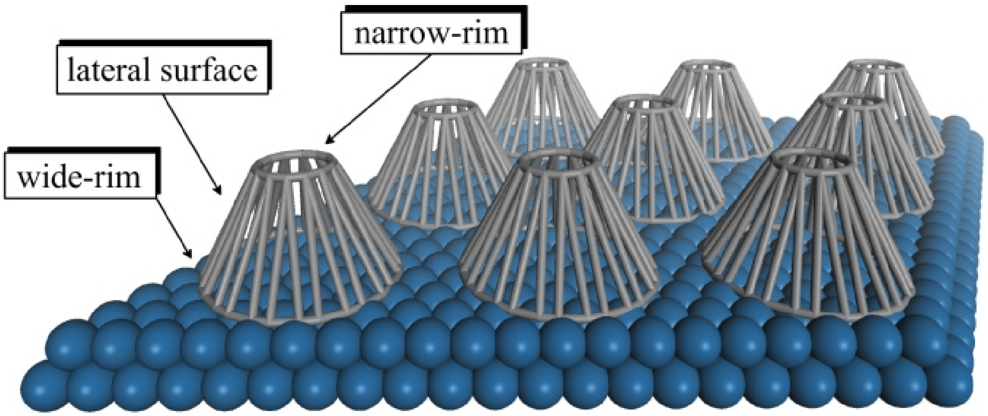
Cyanide adlayer forms (2√3x 2√3)R30º structure on Pt (111)
Itaya et al. J.Am.Chem.Soc. 118 (1996) 393

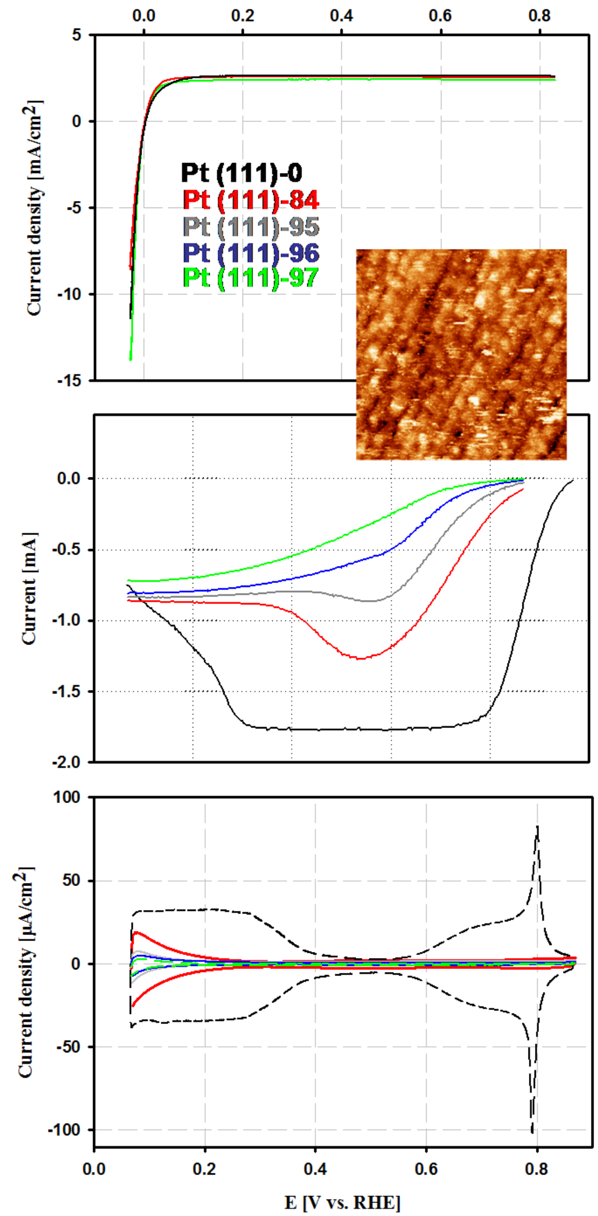




Cyanides prevent the adsorption of sulfates/phosphates

SELECTIVITY: *Pt-calix[4]arene Surfaces*





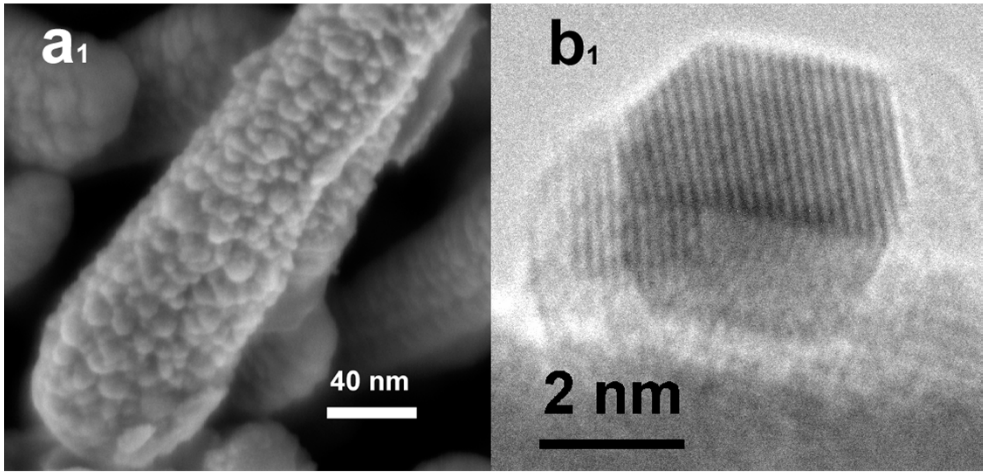
Pt(111)-calix[4]arene surface:

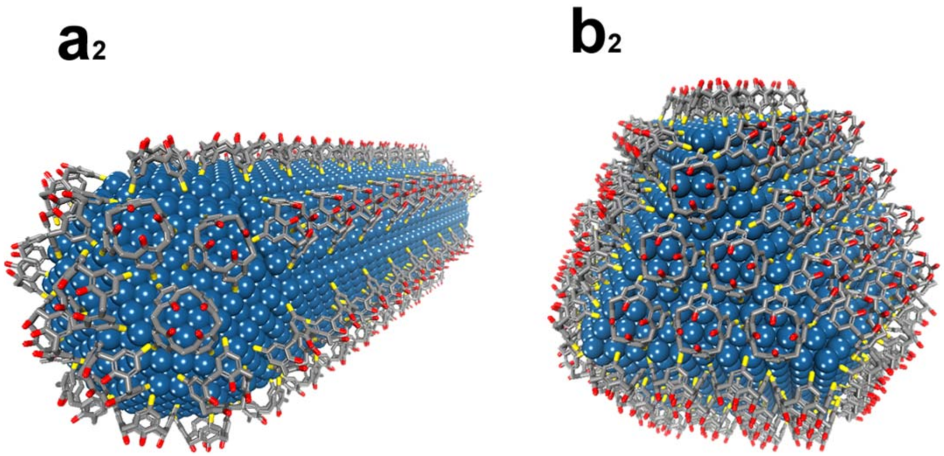
Chemisorbed calix[4]arenes serve as molecular sieves

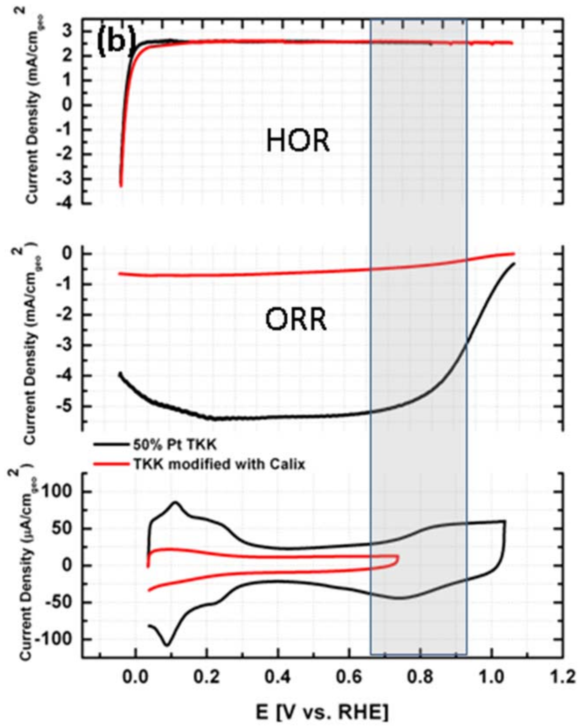
HOR is unaffected

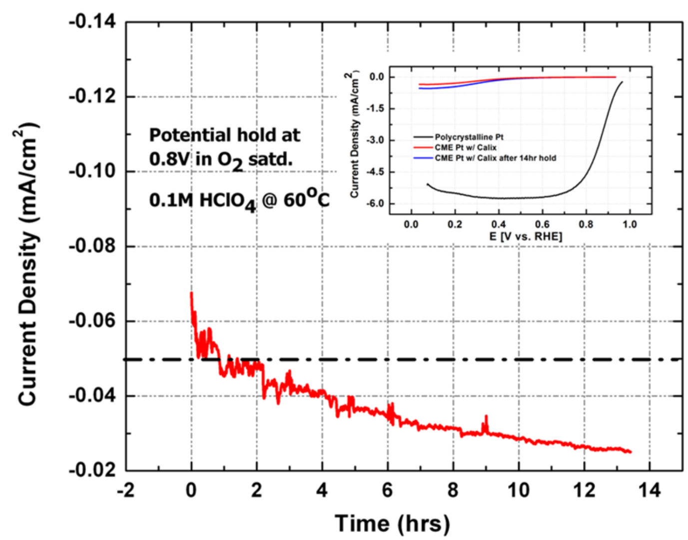
ORR rate is very slow

SELECTIVITY: *Nanoscale Catalysts*

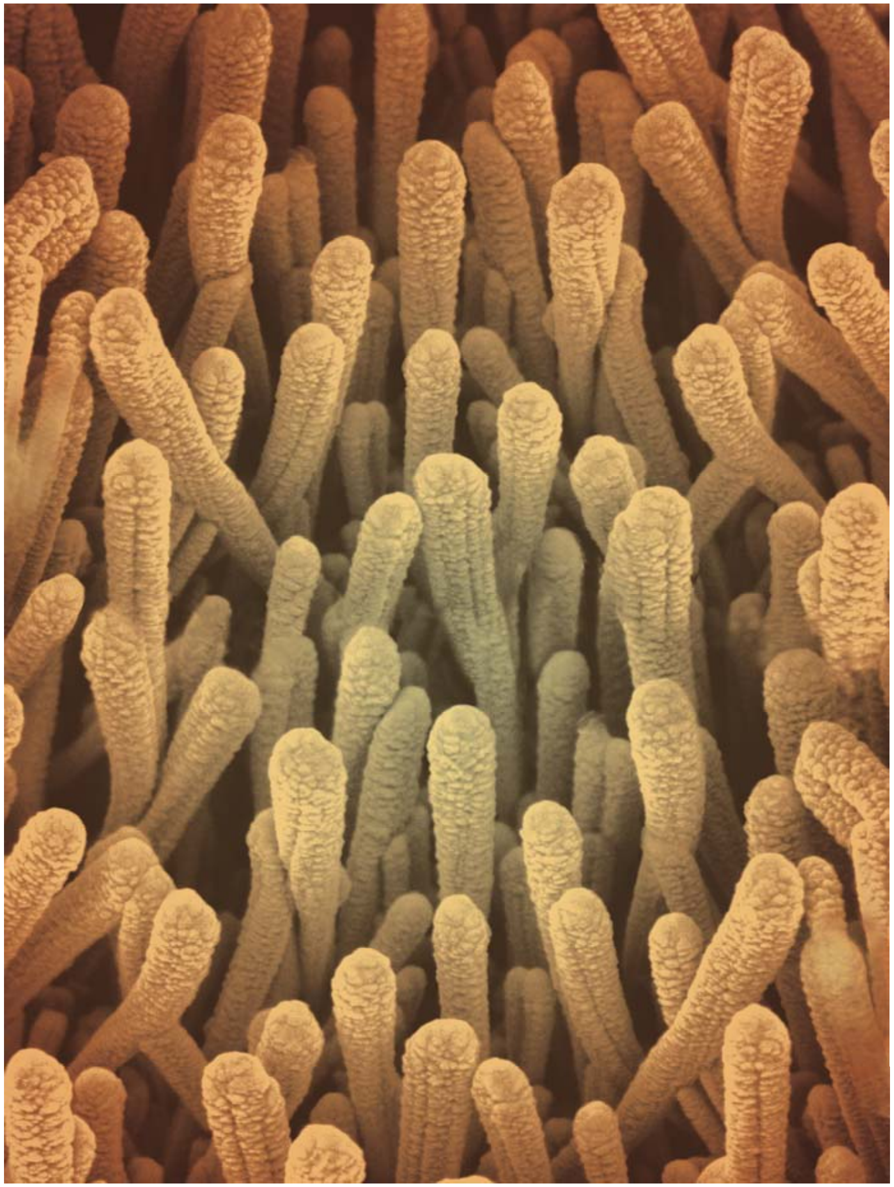






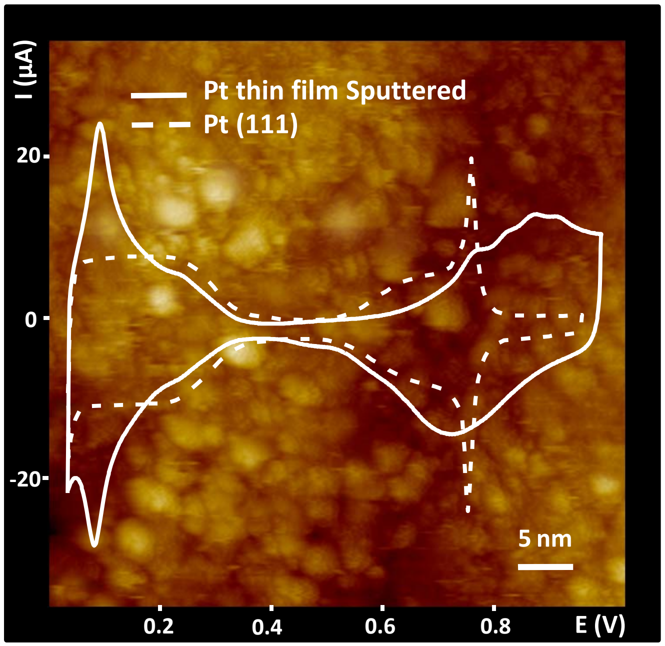


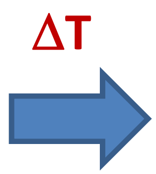
Tailored Electrocatalysts: *Thin Film Based Materials*

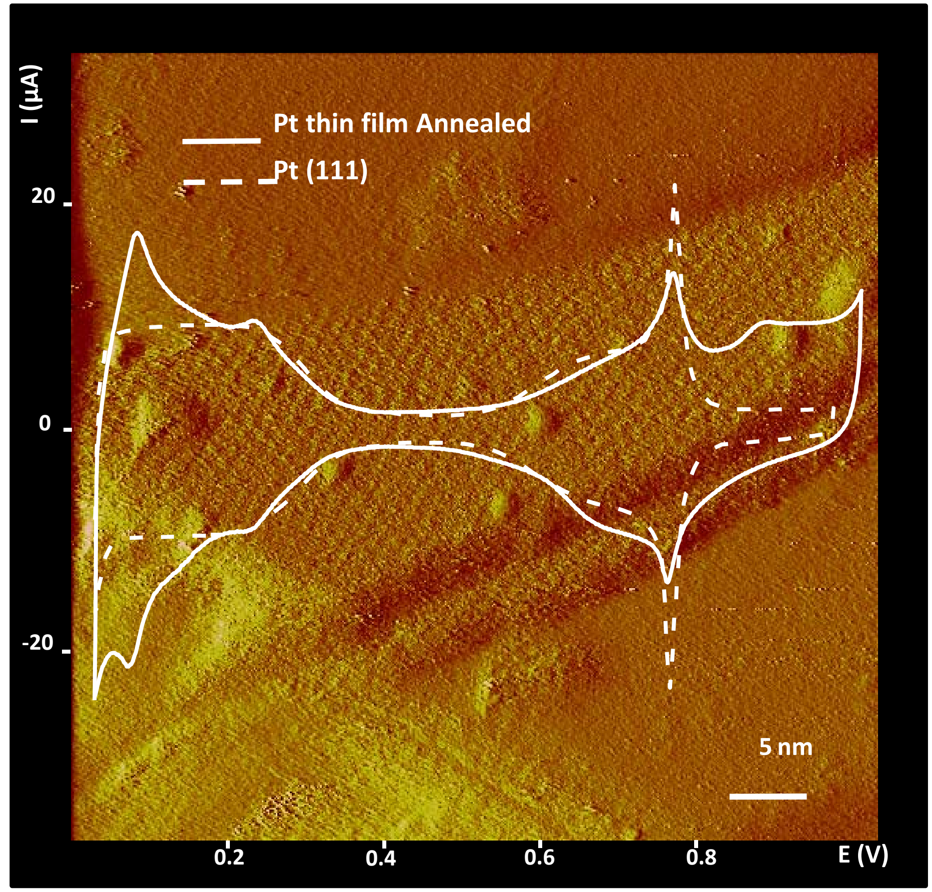


- The surface morphology of the thin film catalyst coating is material and process dependent
- The volume of the catalyst coating depends on the material density and mass loading
- Total loading of precious metals can be optimized
- Segregation profile can be tuned
- Surface morphology can be altered

TAILORING THE STRUCTURE: *Pt-Thin Films*

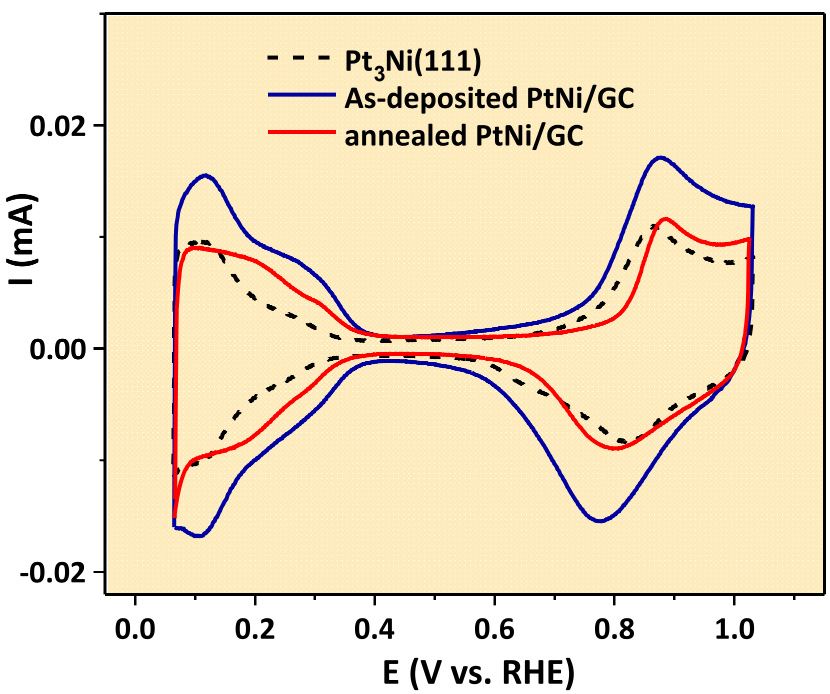


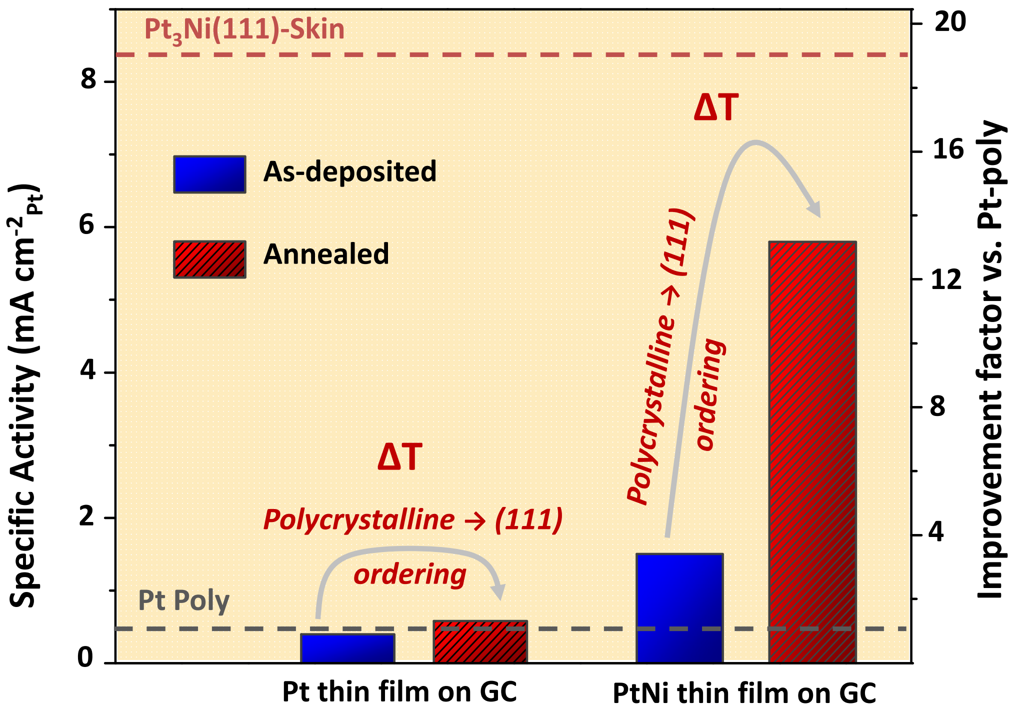




- Magnetron Sputtering Deposition
- Glassy Carbon Support

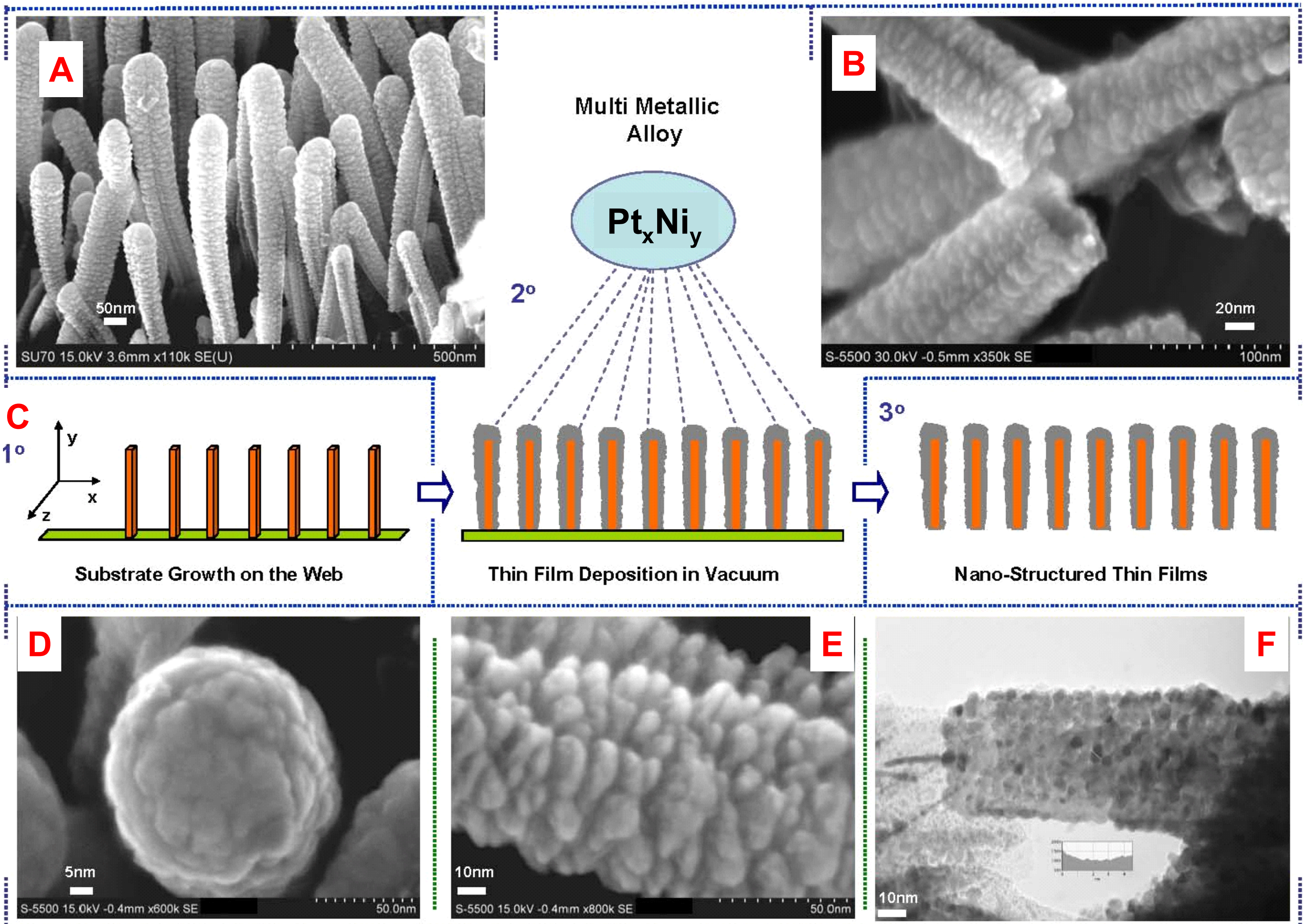
TAILORING THE STRUCTURE and COMPOSITION: *Pt-Bimetalic Thin Films*



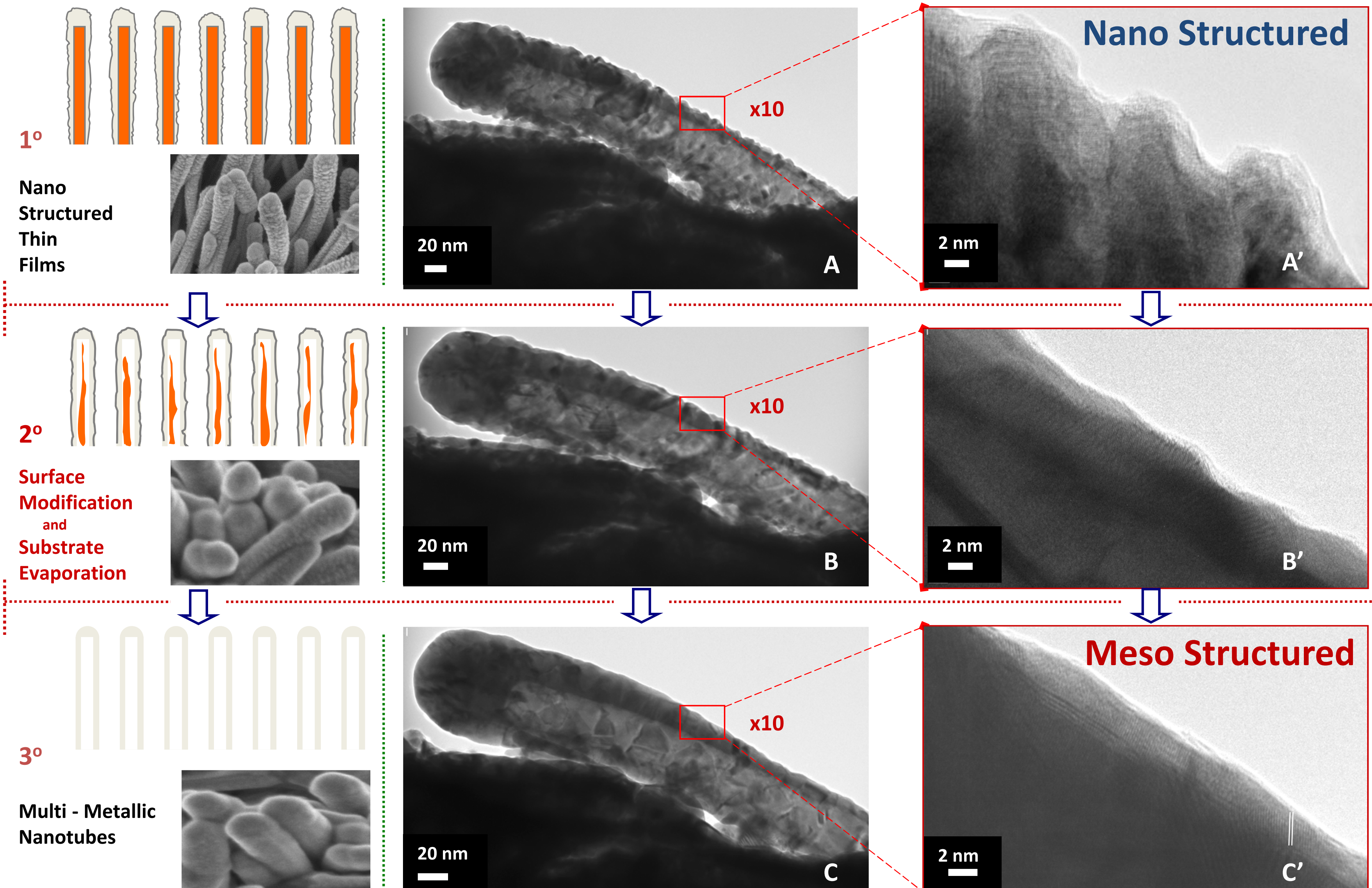


- RDE
- ORR @ 0.95V vs. RHE

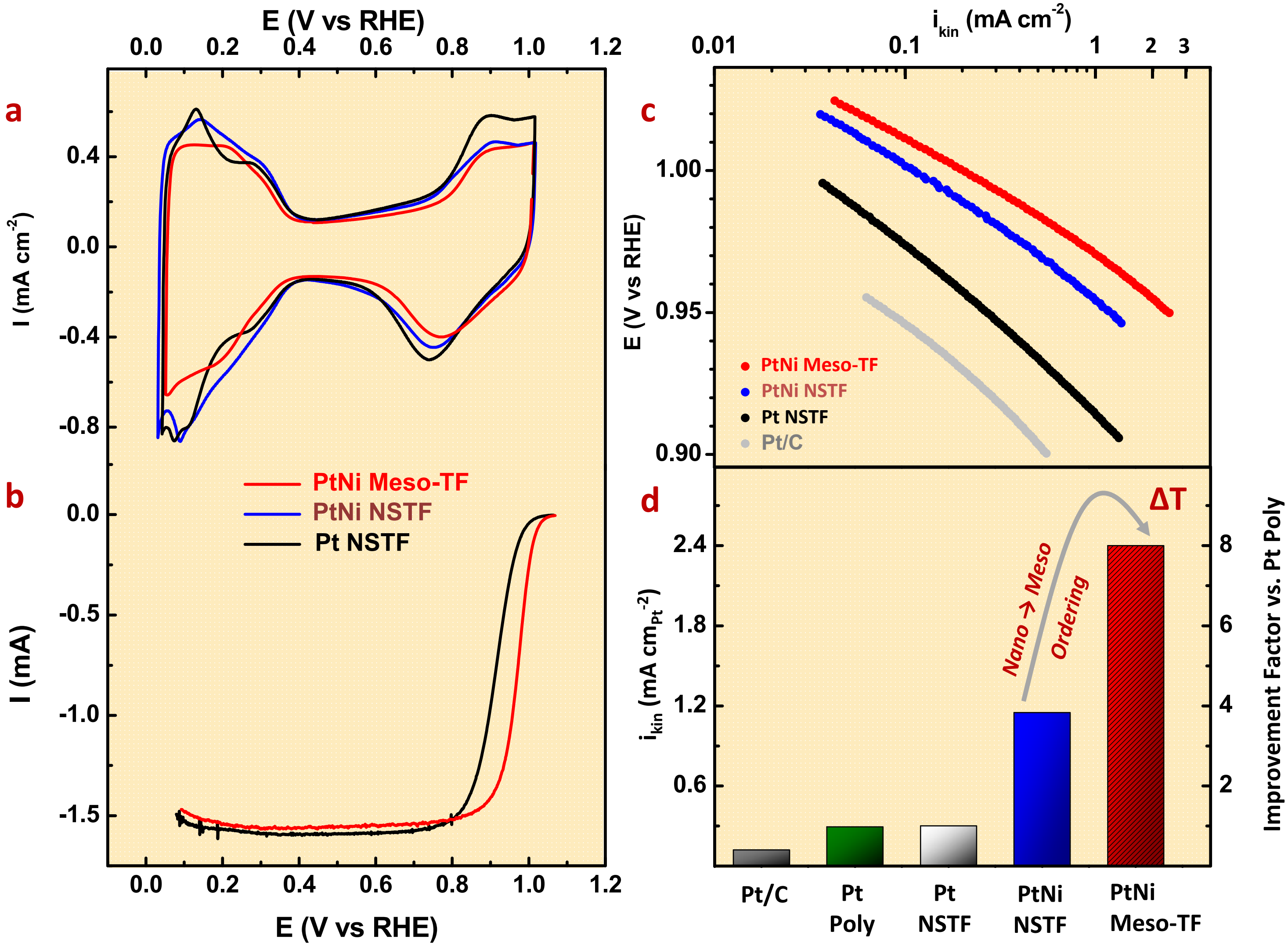
NanoStructured Thin Film Catalysts: *Adjustable Composition*



NSTF: *Surface Modification*

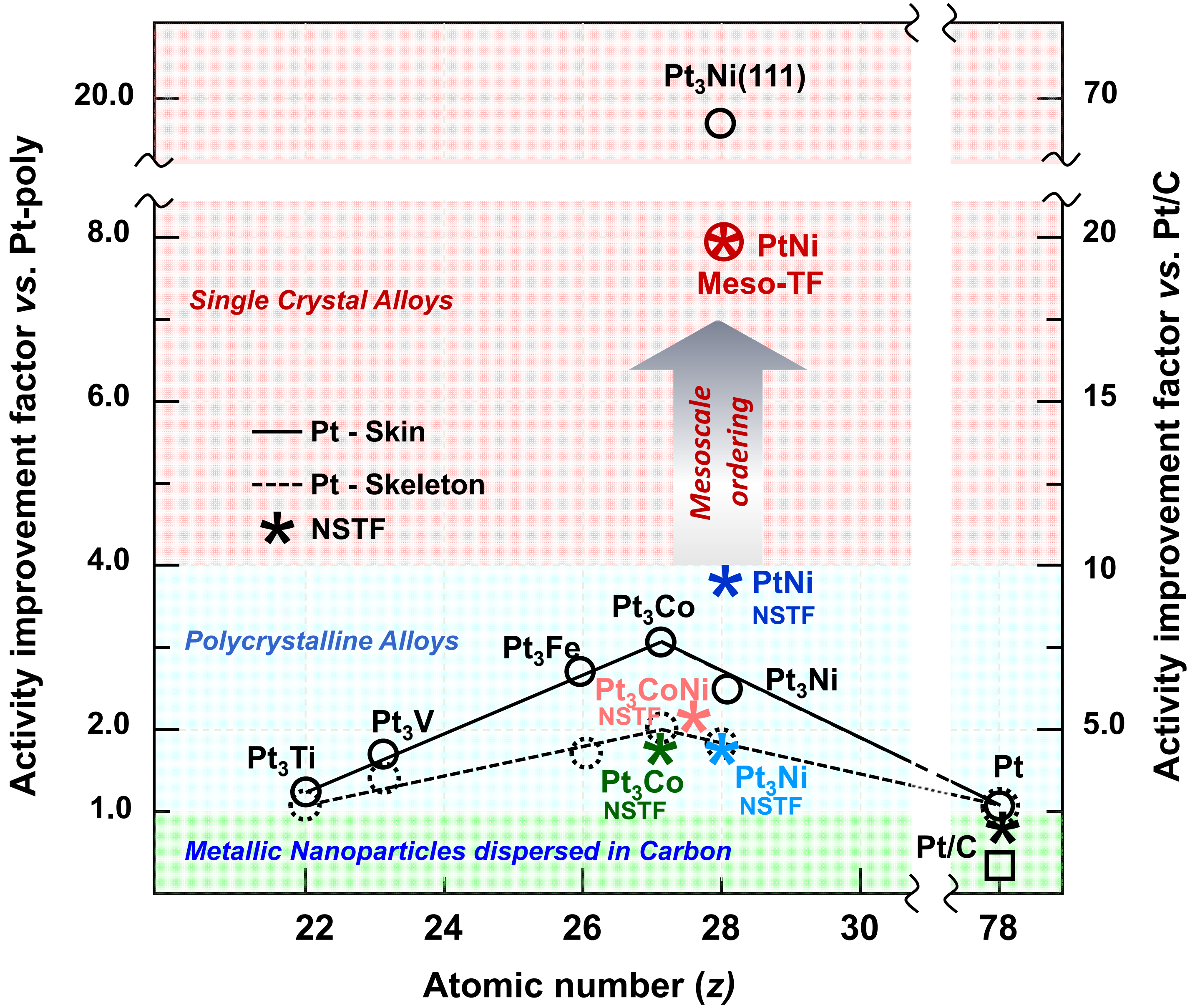


MESOSTRUCTURED ELECTROCATALYSTS: *Thin Film Based Materials*



- RDE
- ORR @ 0.95V vs. RHE

Activity Map for the ORR: *Pt and Pt alloys*



ADVANCED ELECTROCATALYSTS SUMMARY

- Rational design and synthesis based on well-defined systems

- Control of critical parameters: particle size, compositional profile, surface structure

- Utilization of superior catalytic properties of Pt-Skin surfaces at nanoscale

- NPs with one order of magnitude catalytic enhancement for the ORR

- Highly durable multimetallic NPs

- Electrocatalysts with modified surfaces by self assembled monolayers

- Selective electrocatalysts for utilization as anode in PEM Fuel Cells

- Mesostructured thin films as electrocatalysts with tunable surface structure

- First practical catalysts with catalytic properties that can approach bulk materials

- 20-fold enhancement in catalytic activity for the ORR

Collaborators

Oak Ridge National Laboratory

Toyota R&D Labs

Brown University

University of Pittsburgh

General Motors

3M

Nissan

Jet Propulsion Lab

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Relevant Publications

C. Wang, D. van der Vliet, K.C. Chang, H. You, D. Strmcnik, J.A. Schlueter, N.M. Markovic, V.R. Stamenkovic
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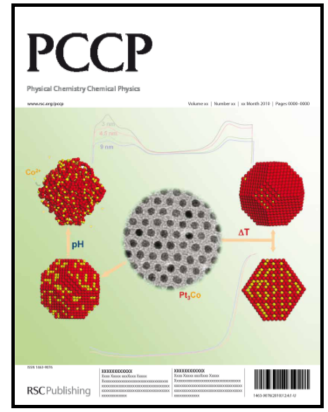
J. Phys. Chem. C., 113(2009)19365



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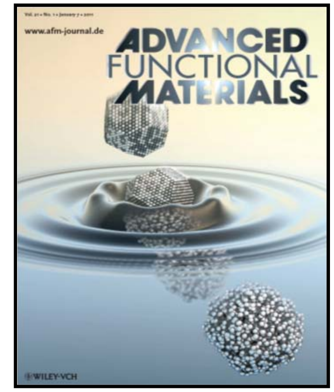

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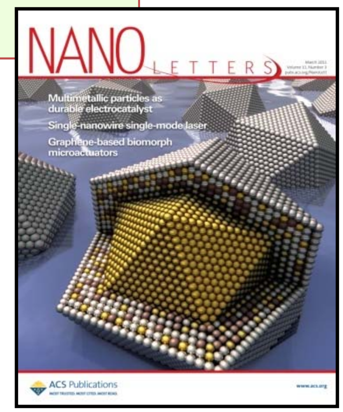

C. Wang, D.van derVliet, K.L. More, N.J. Zaluzec, S. Peng, S. Sun, H. Daimon, G. Wang, J. Greeley, J. Pearson, A.P. Paulikas, G. Karapetrov, D. Strmcnik, N.M.Markovic, V.R.Stamenkovic
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C. Wang, M.Chi, D. Li, D. Strmcnik, D.van derVliet, G. Wang, V. Komanicky, K.-C. Chang, A.P. Paulikas, D. Tripkovic, J. Pearson, K.L. More, N.M.Markovic, V.R.Stamenkovic
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Electrochimica Acta, 56,24(2011)8695

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Mesostructured Thin Films as Electrocatalysts with Tunable Composition and Surface Morphology
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