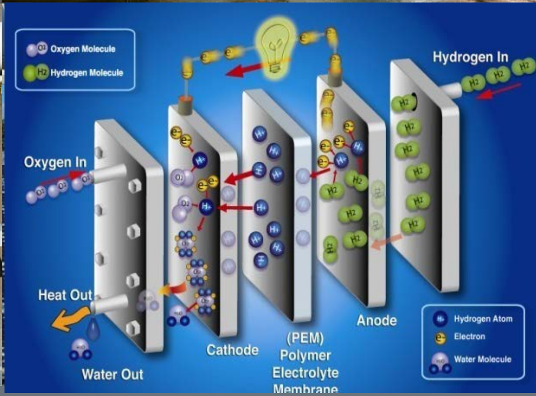
FCTO Monthly Webinar Series:

# Past, Present and Future Challenges in Electrocatalysis for Fuel Cells

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy





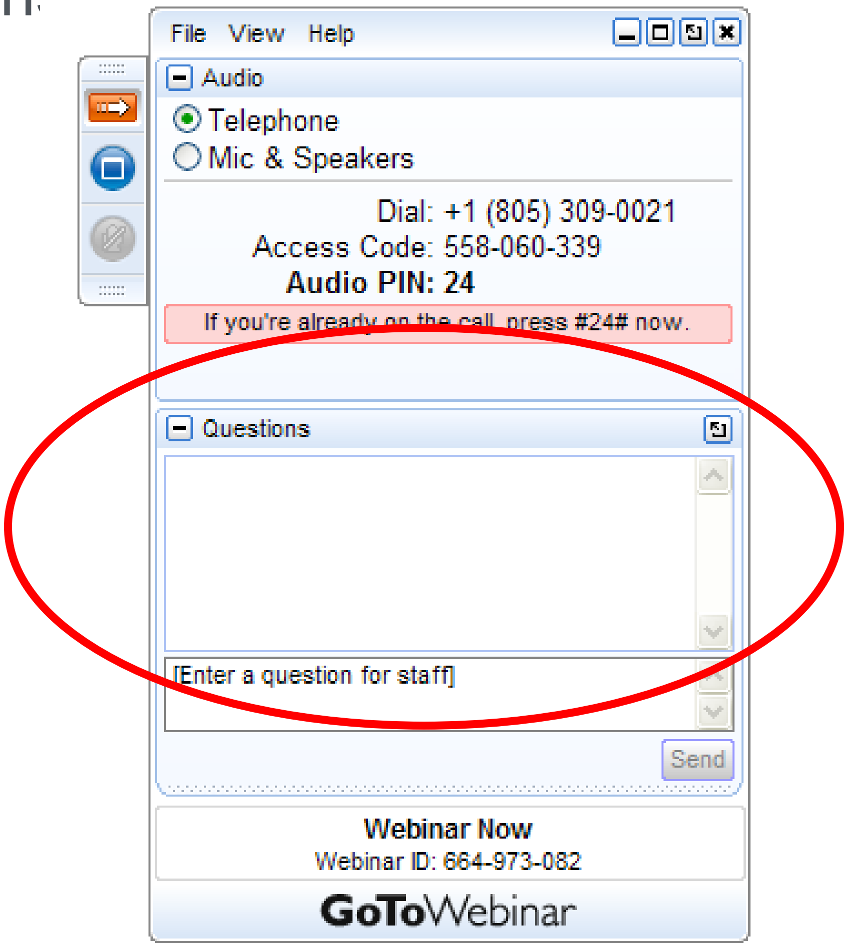

Presenter:
Voya (Vojislav) Stamenkovic
*Argonne National Laboratory*

DOE Host:
Dimitrios Papageorgopoulos
*Fuel Cell Technologies Office*

**U.S. Department of Energy**
**Fuel Cell Technologies Office**
**October 13th, 2016**

# Question and Answer

- Please type your questions into the question box



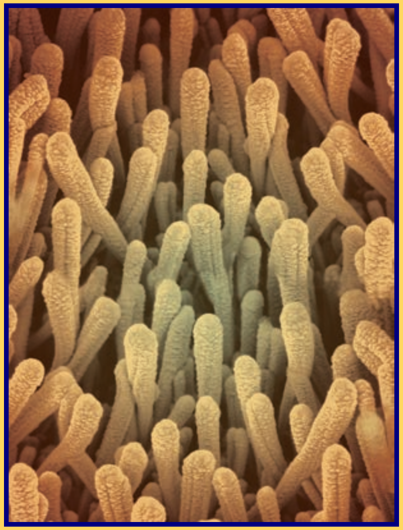
Argonne NATIONAL LABORATORY

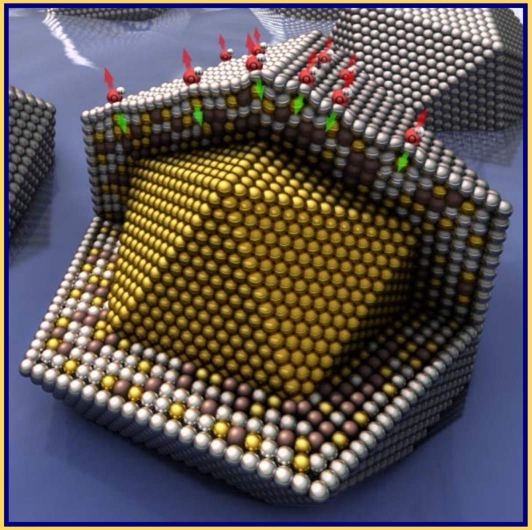
*... for a brighter future*

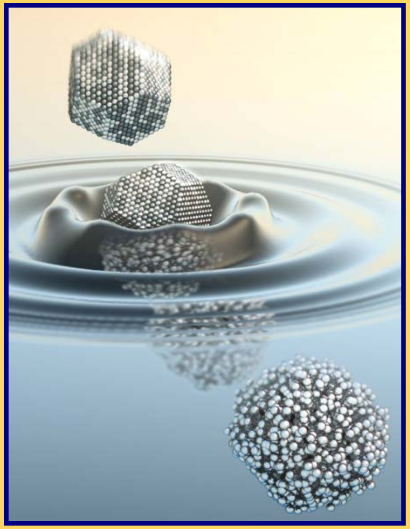
# Past, Present and Future Challenges in Electrocatalysis for Fuel Cells


**Materials Science Division**
**Argonne National Laboratory**

**Vojislav Stamenkovic**





**DOE EERE Fuel Cell Technology Office Webinar Series**

October 13, 2016


U.S. Department of Energy

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U.S. DEPARTMENT OF ENERGY

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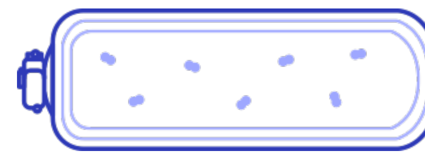
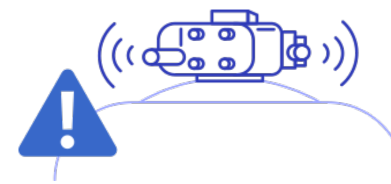
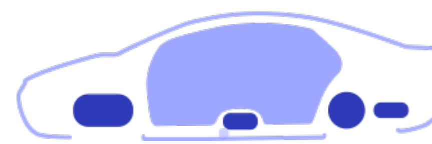
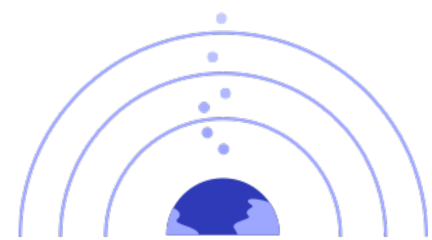
https://www.toyota.com/mirai/fcv









# 2016 Toyota Mirai

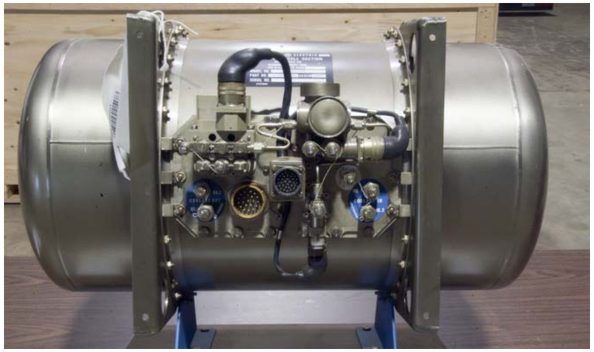
**$499/month  36-month lease**
**$57,500 MSRP**

**HYDROGEN SAFETY**
**Science behind the safety**
Safety was our primary objective when we engineered the Mirai. Our proprietary safety system is based on four fundamental principles.

**The first production fuel cell vehicle**

The Mirai is at the forefront of a new age of hydrogen fuel cell cars that allows you to enjoy long distance zero-emissions driving. As well as only producing water from its tailpipe – which means no impact on our planet when you're driving – Mirai brings the unique Toyota Hybrid driving experience to a new level.

’60s

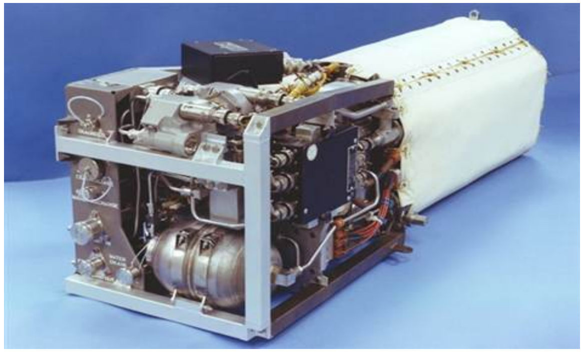


PEM FC
unsupported Pt catalyst
loading: 28 $mg_{Pt}/cm^2$
membrane: Nafion
T ~ 21°C

’60-70s

Alkaline FC
Ni based catalyst
T ~ 250°C
Operating time: 400-690h

’80-2011



Alkaline FC
Pt and PtAu catalysts
loading: 10 and 20 $mg_{Pt}/cm^2$
T ~ 93°C
Operating time: > 16 days

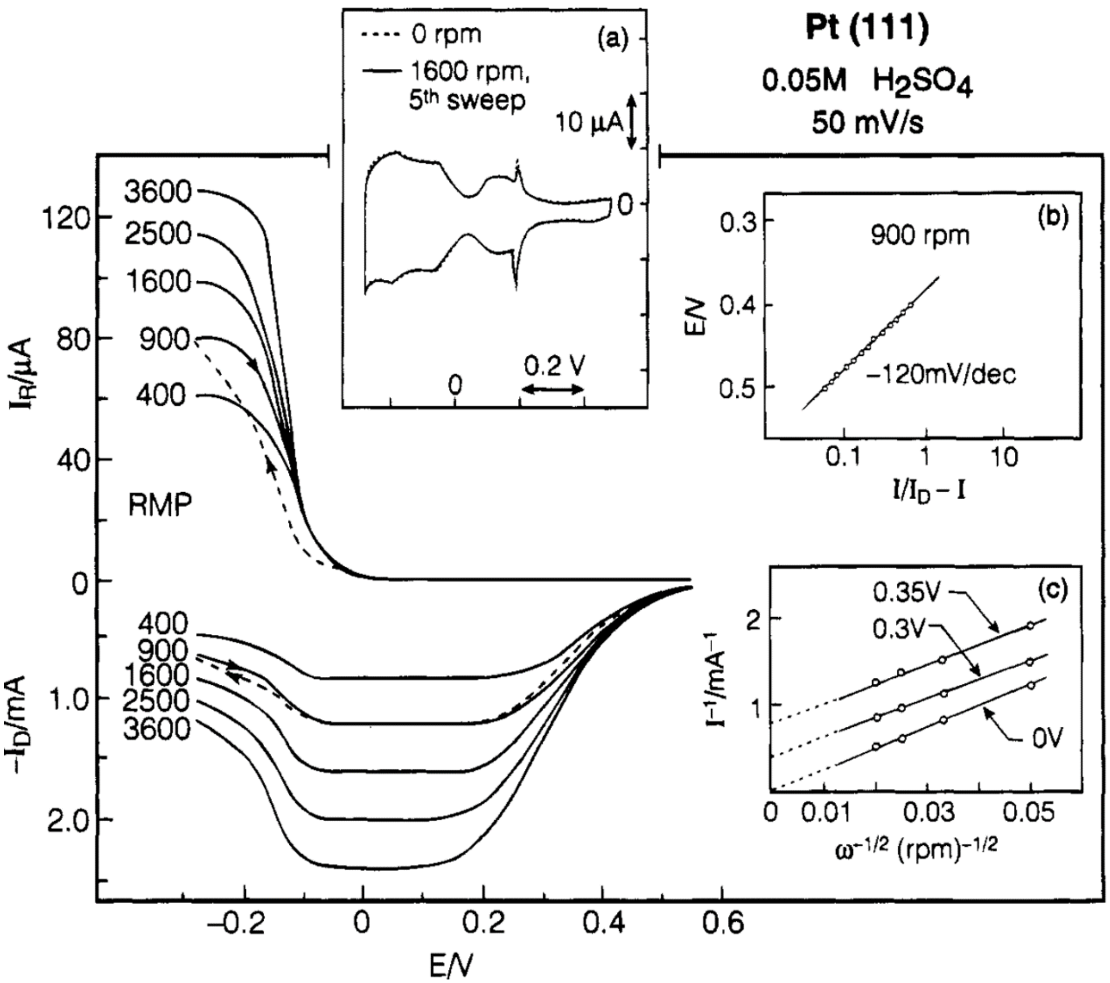
# Oxygen Reduction on Platinum Low-Index Single-Crystal Surfaces in Sulfuric Acid Solution: Rotating Ring−Pt(*hkl*) Disk Studies

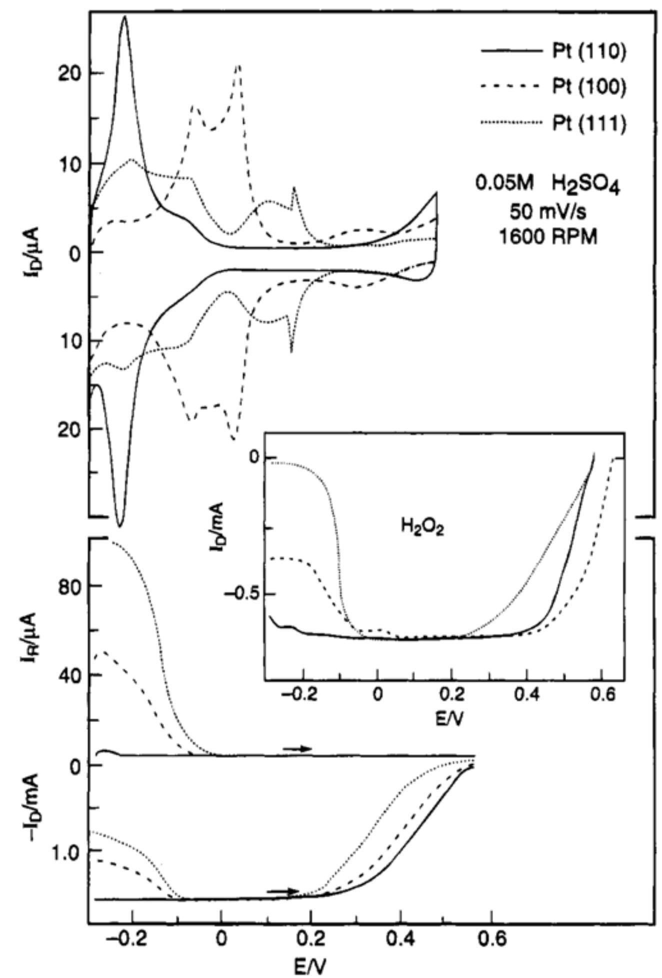
**Nenad M. Marković,* Hubert A. Gasteiger, and Philip N. Ross, Jr.**

*Materials Science Division, Lawrence Berkeley Laboratory, Berkeley, California 94720*

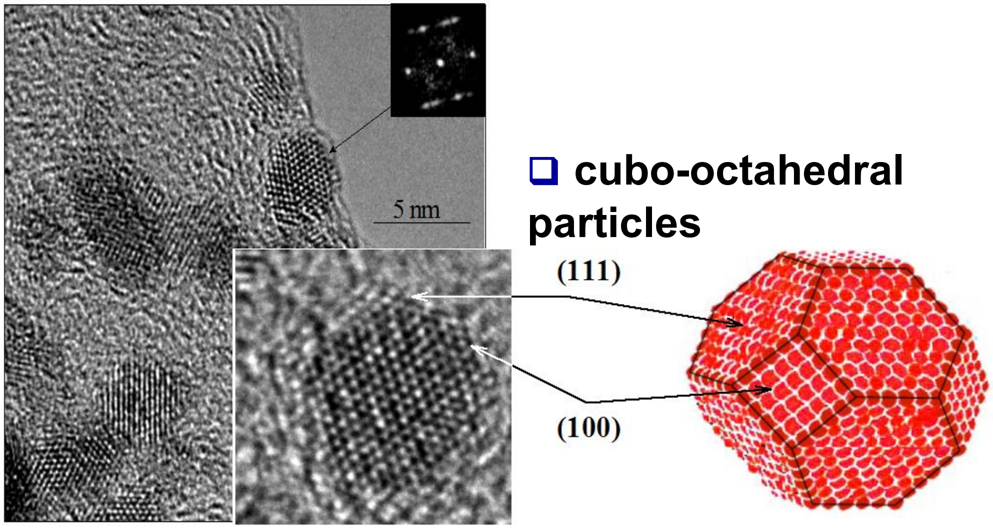
*Received: September 28, 1994; In Final Form: December 16, 1994*[⊗]

**3414** *J. Phys. Chem., Vol. 99, No. 11, 1995*



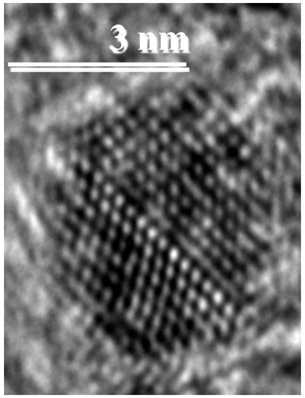



# Particle Size Effect

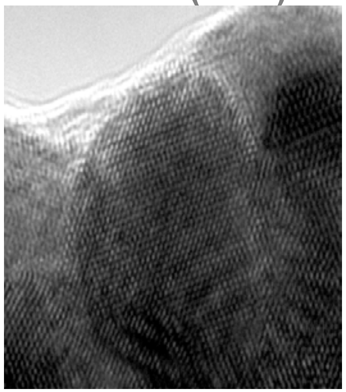


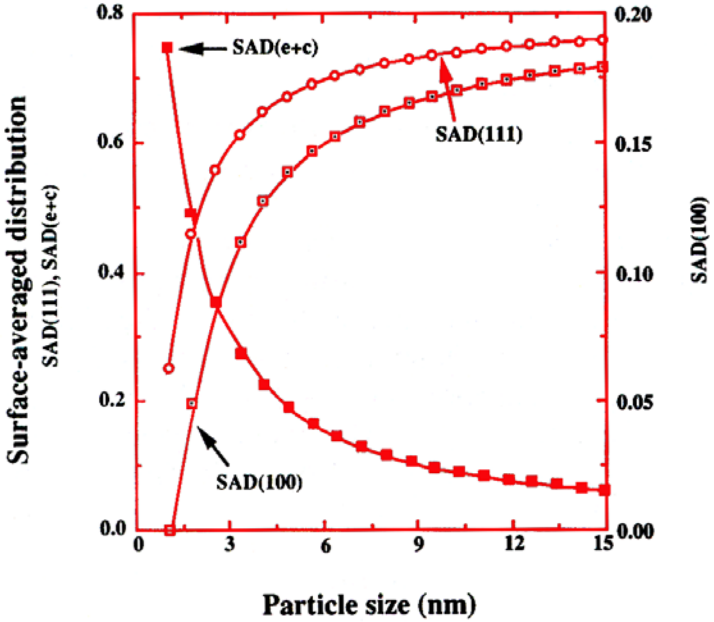

- cubo-octahedral particles

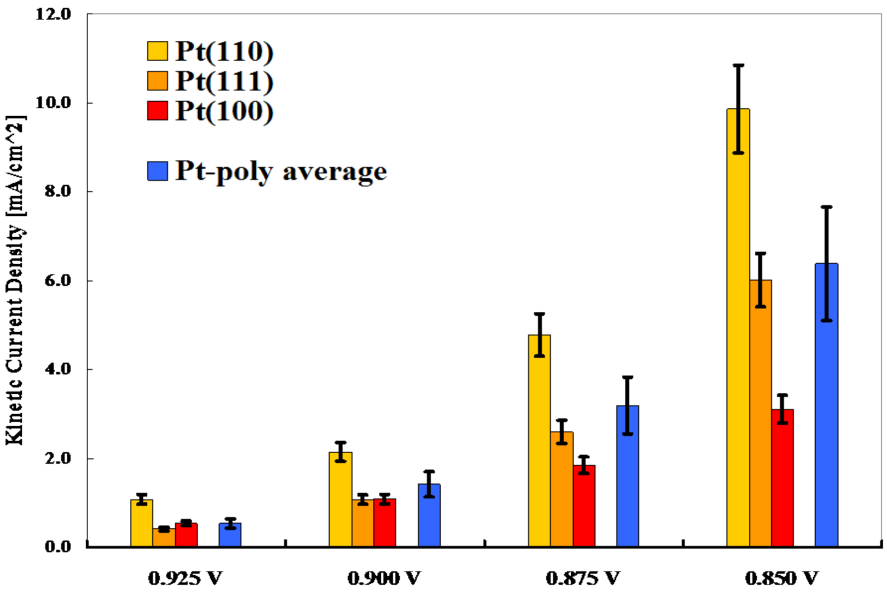
10 % Pt/Vulcan




30 nm (Pt/C)



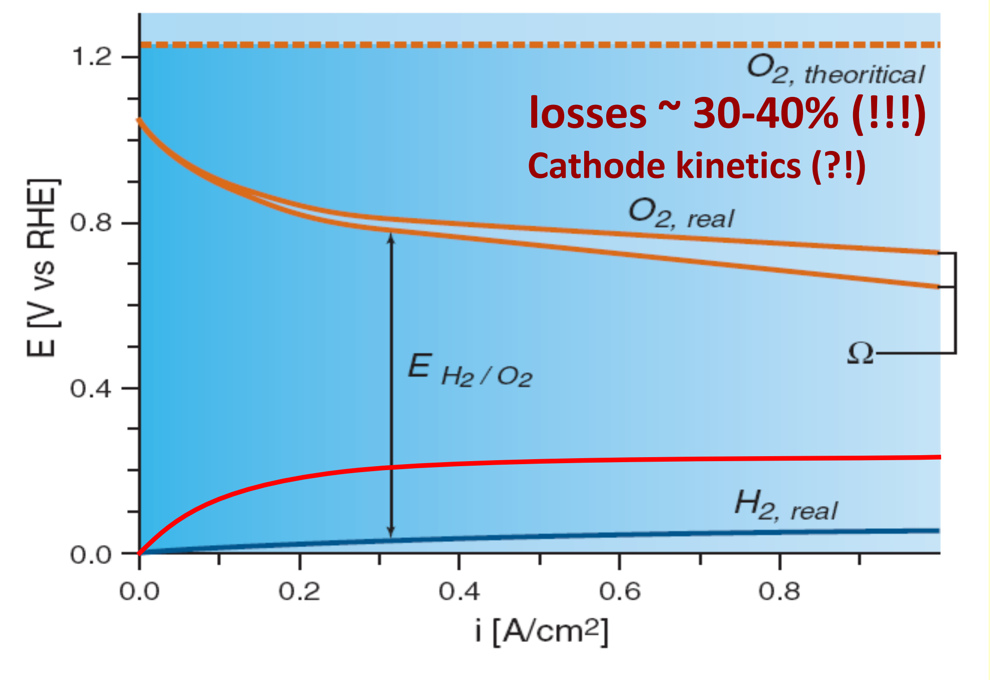


# ORR: *cathode limitations*

## 2020 DOE Technical Targets

- Mass activity @0.9V: 0.44 $A/mg_{Pt}$
- Electrochemical area loss: < 40%
- PGM Total content: 0.125 g/kW
- PGM Total loading: 0.125 $mg/cm^2_{electrode}$
- Durability w/cycling (80$^o$C): 5000 hrs




**Main limitations in PEM fuel cell technology:**

1) **Activity:** Pt/C = Pt-poly/10

2) **Durability:** (Pt catalyst dissolves)

3) **Pt loading:** Cost Issues

**Activity | Durability | Cost**

Specific/Mass Activity | Electrochemical Stability | Loading

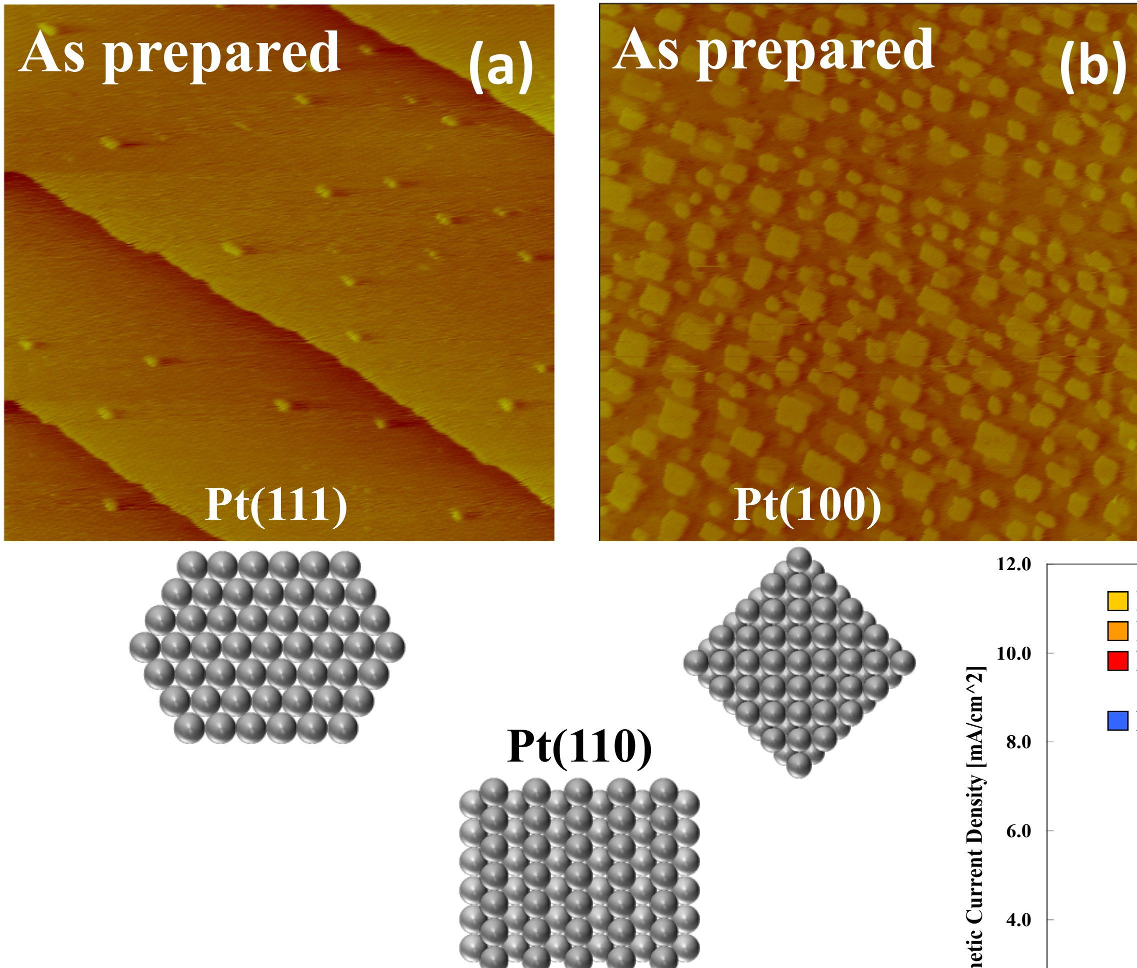
1° Structure-Function

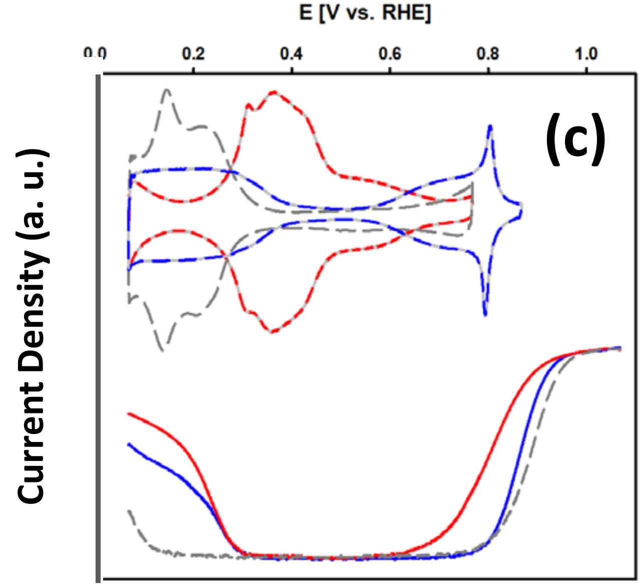
2° Composition-Function

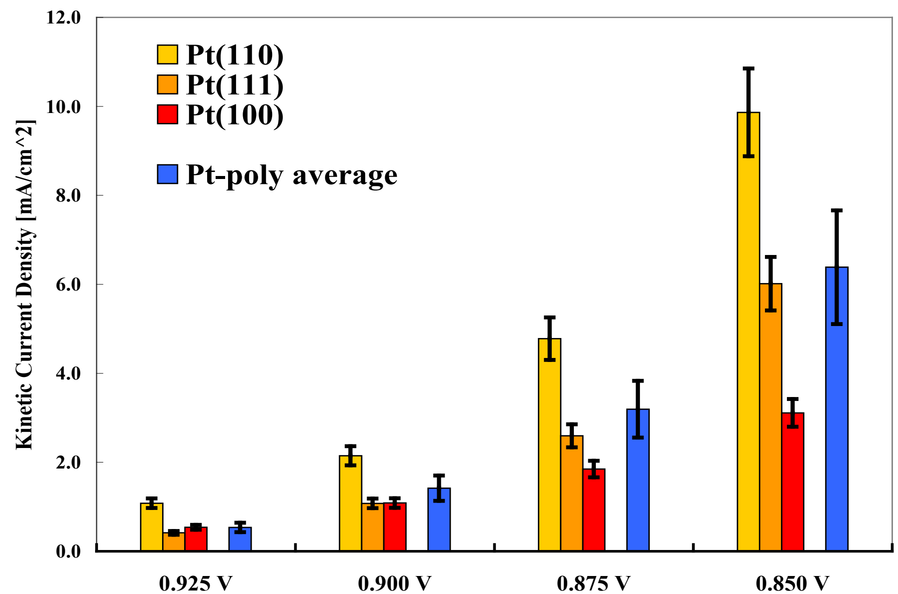
3° Surface Modifications

4° Tailored Electrolytes

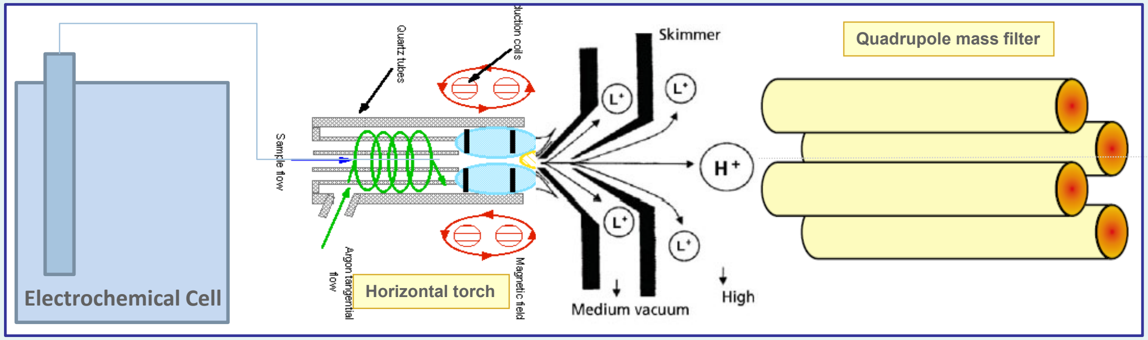
# STM: *Pt Single Crystals*



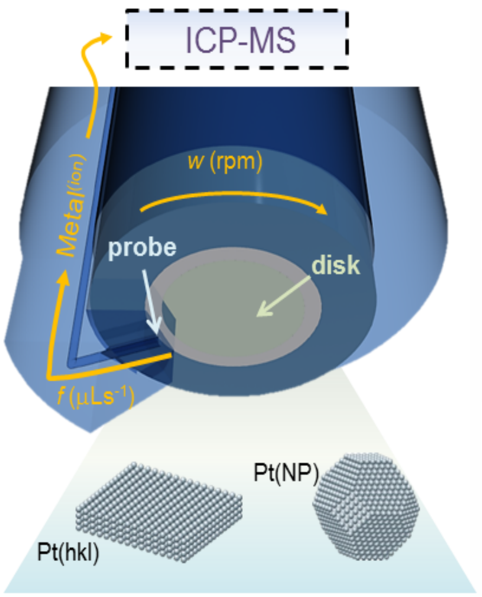



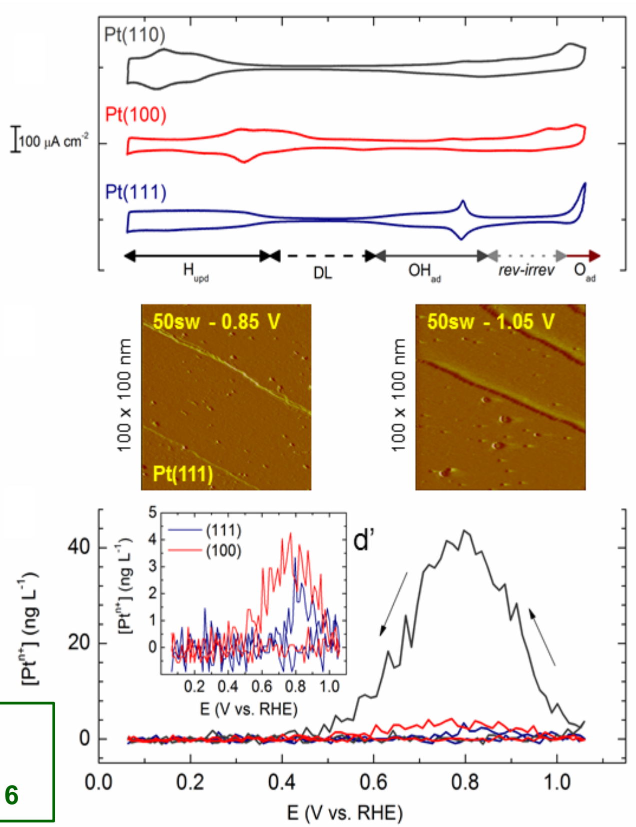
# *In-Situ EC-ICP-MS* Pt(hkl)-Surfaces vs. **Pt/C**

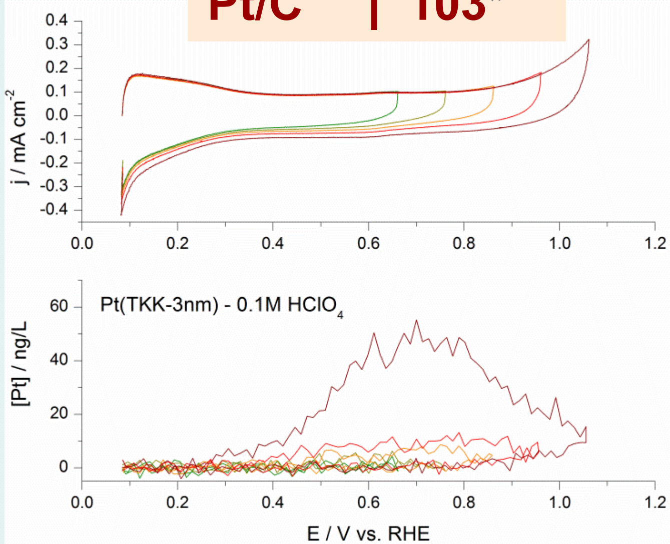



**Total Pt loss over one potential cycle up to 1.05 V for distinct Pt surface morphologies, indicating the stability trend follows the coordination number of the surface sites**

| Pt Surface | Dissolved Pt per cycle [μML] |
|---|---|
| Pt(111) | 2 |
| Pt(100) | 7 |
| Pt(110) | 83 |
| Pt-poly | 36 |
| Pt/C | 103* |



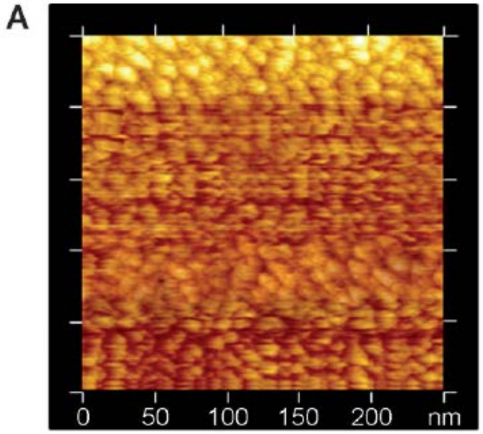



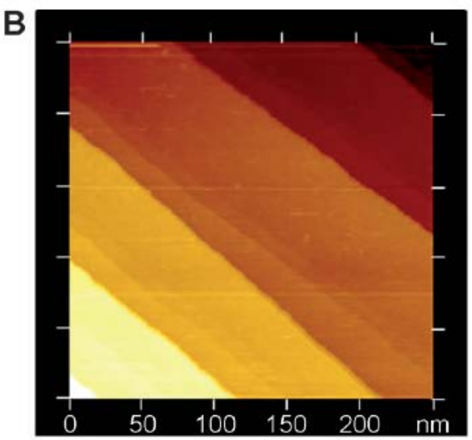

P. P. Lopes, D. Strmcnik, J. Connell,
V. R. Stamenkovic and N.M. Markovic
**ACS Catalysis, 6 (4), 2536-2544, 2016**

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

**STM**

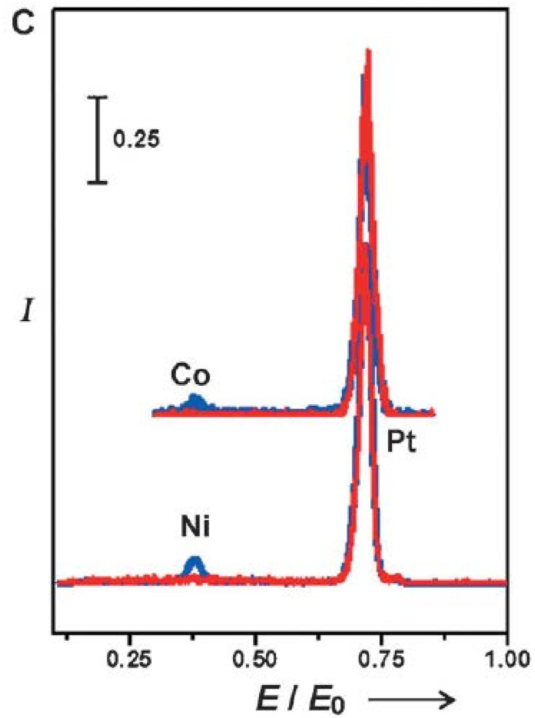


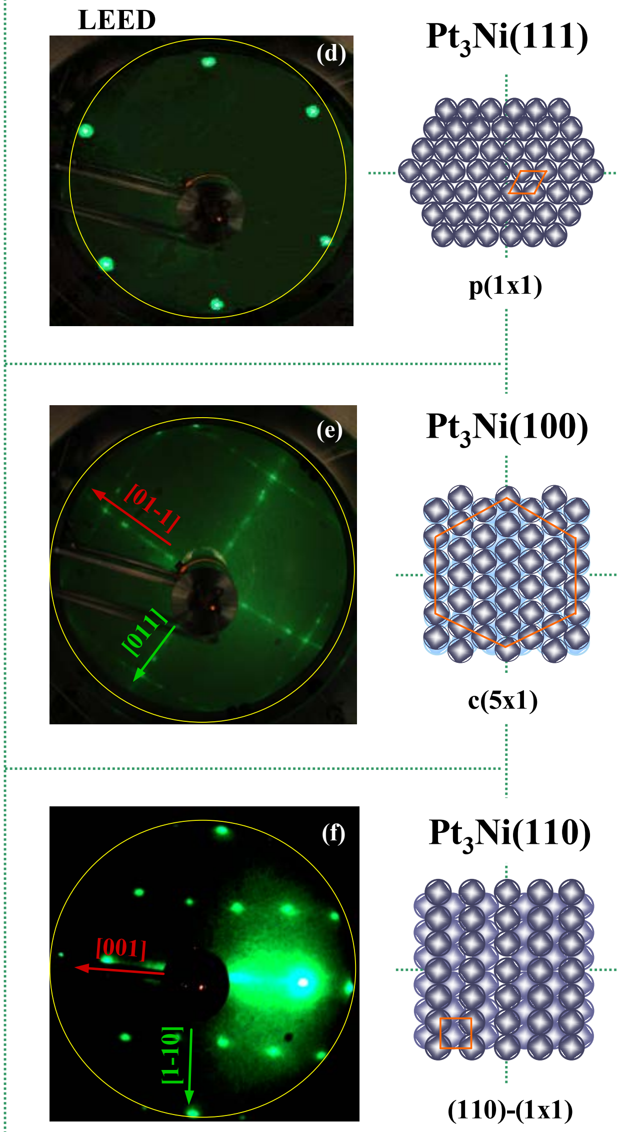

***Sputtered***




***Annealed***

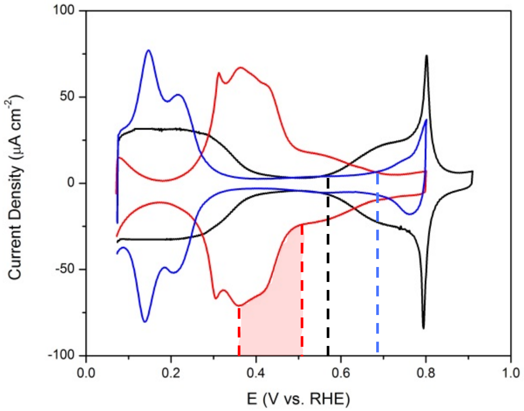
**LEIS**



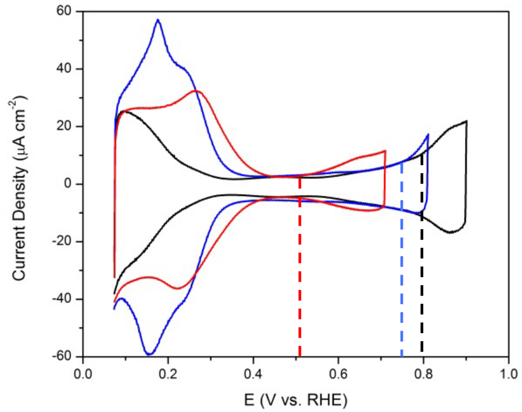



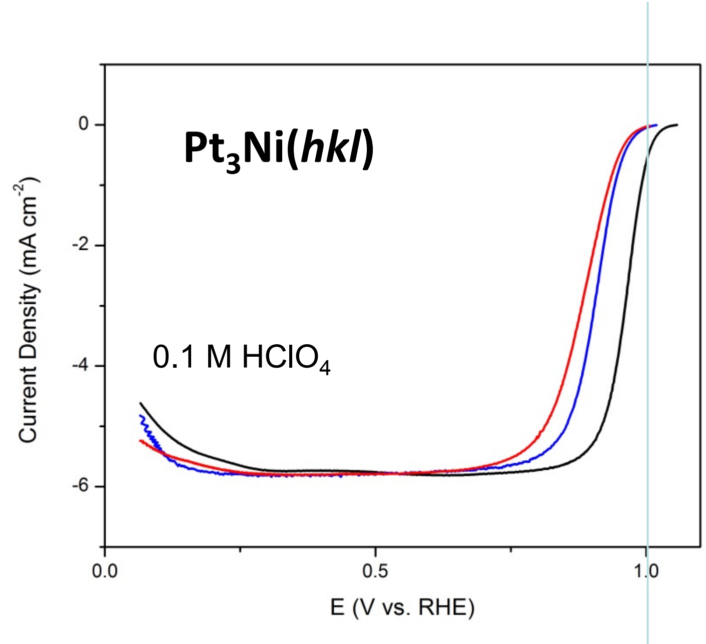
# Activity: *ORR Platinum Alloy Surfaces*

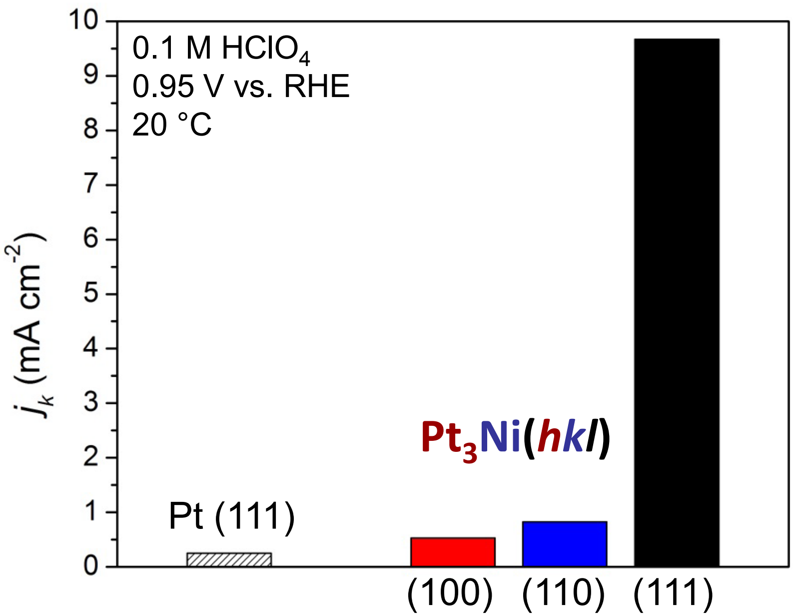
**Pt(*hkl*)**

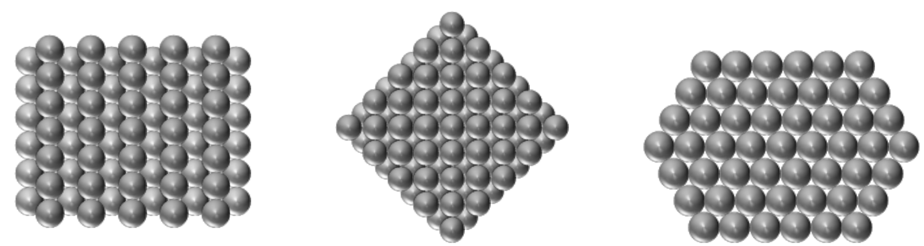



**$Pt_3Ni$(*hkl*)**



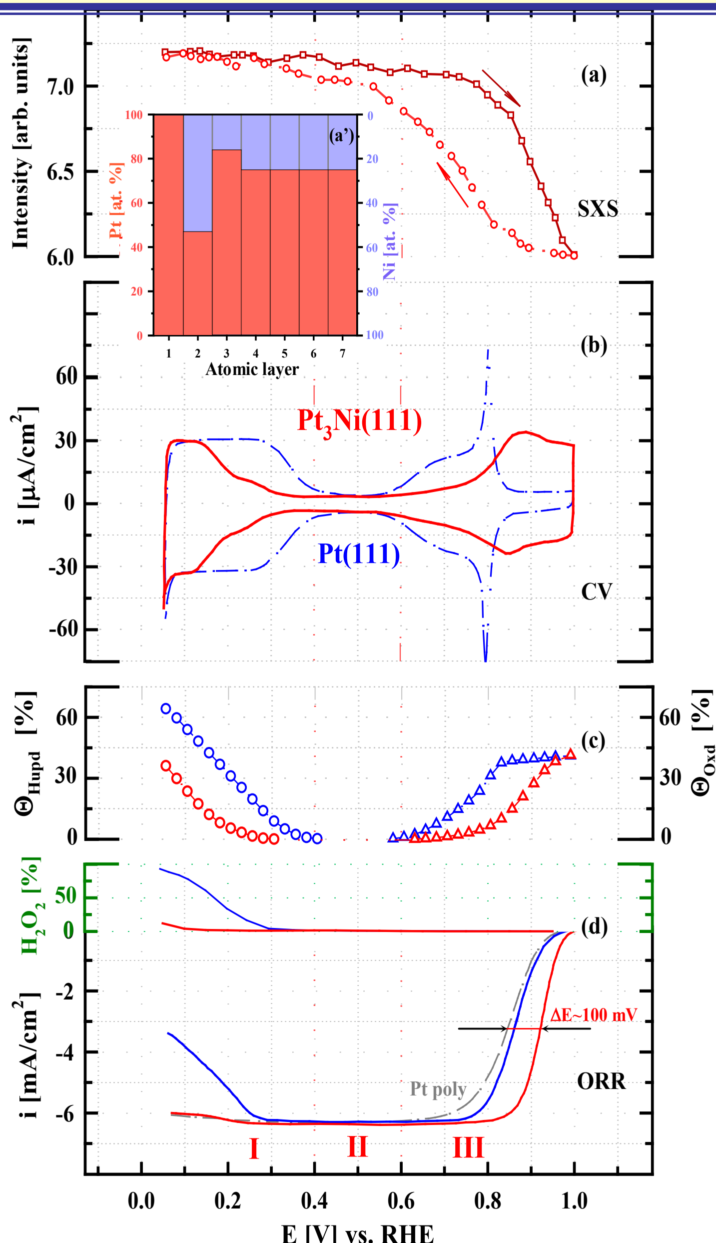



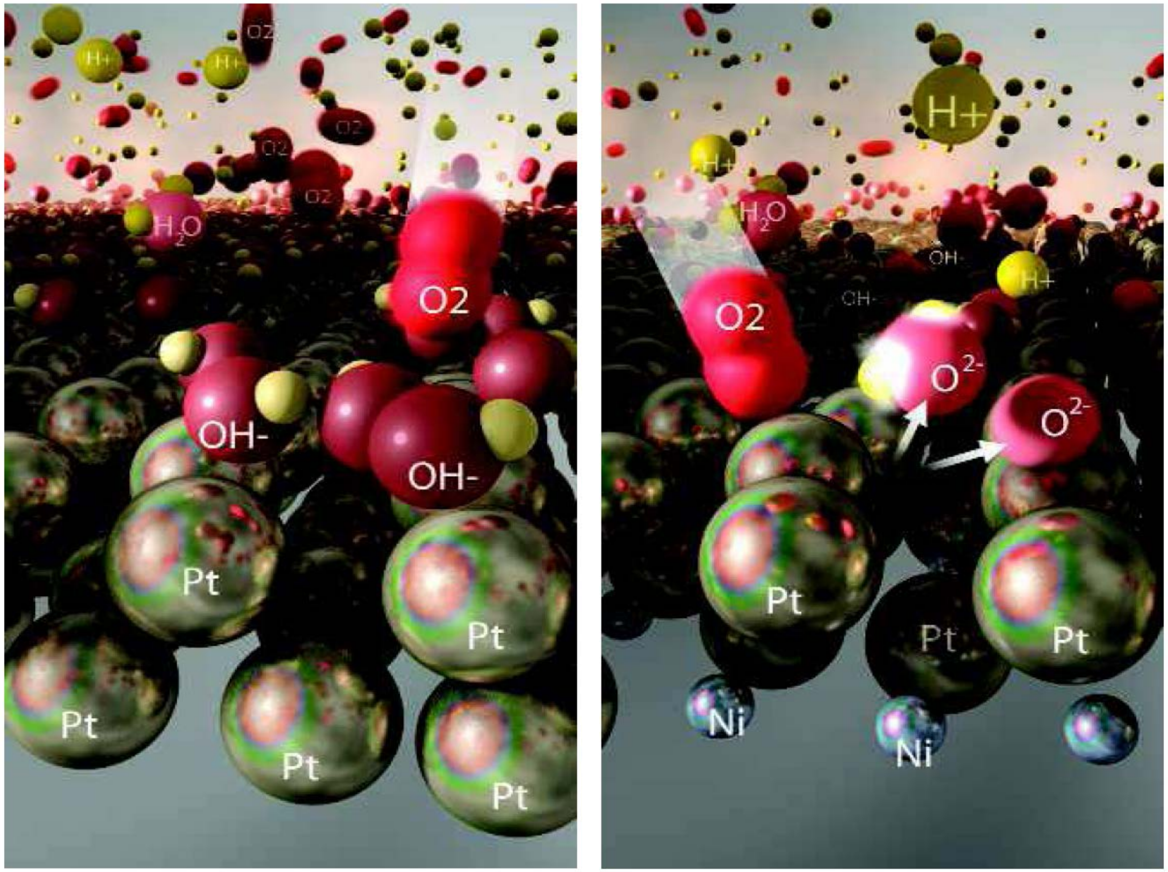



$Pt_3Ni$(110) $Pt_3Ni$(100) $Pt_3Ni$(111)

**$Pt_3Ni$(111)/Pt-Skin Surface is the most active catalyst for the ORR**

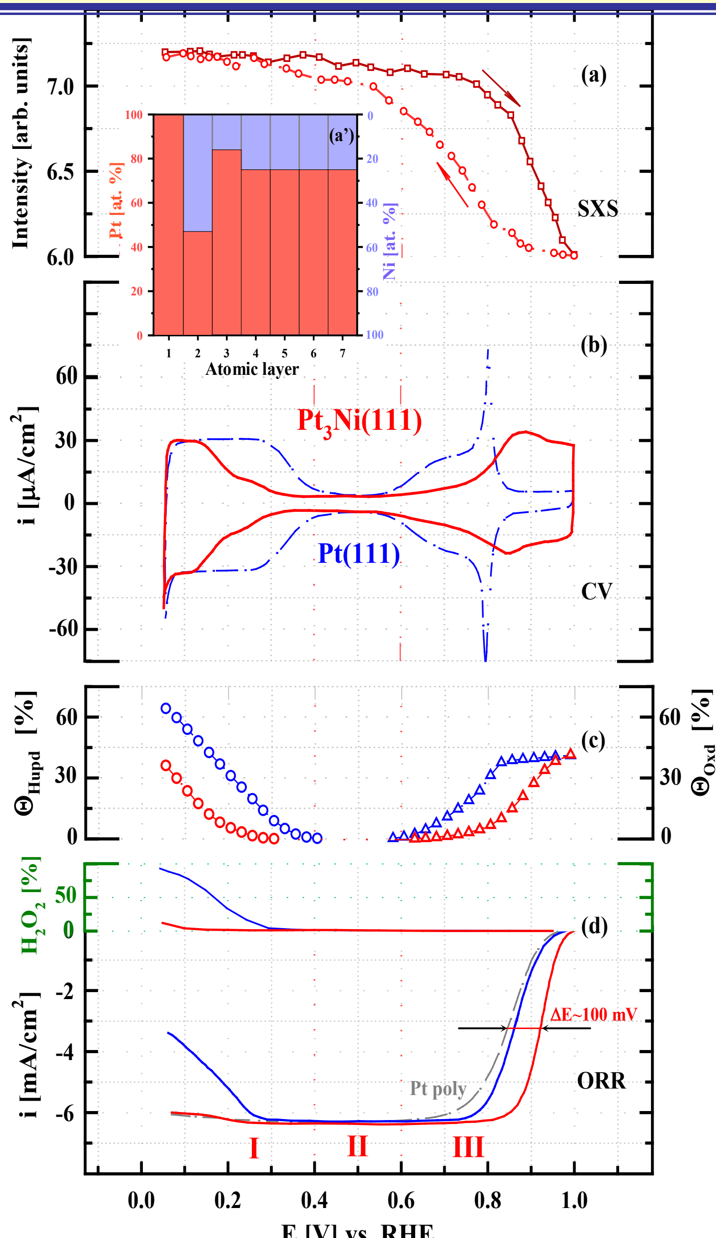
# Subsurface Composition + Surface Structure: *$Pt_3Ni(111)$*

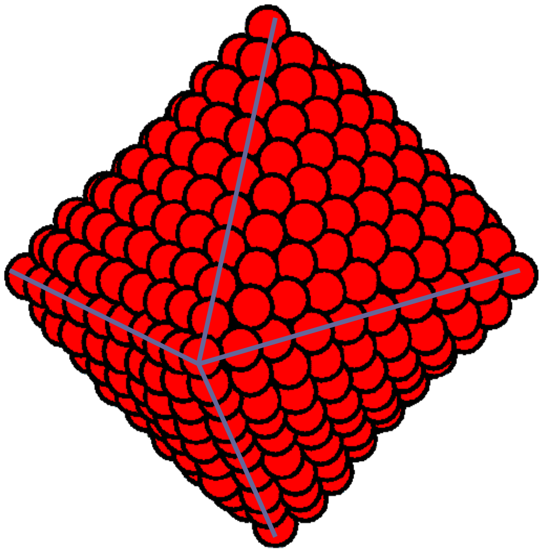


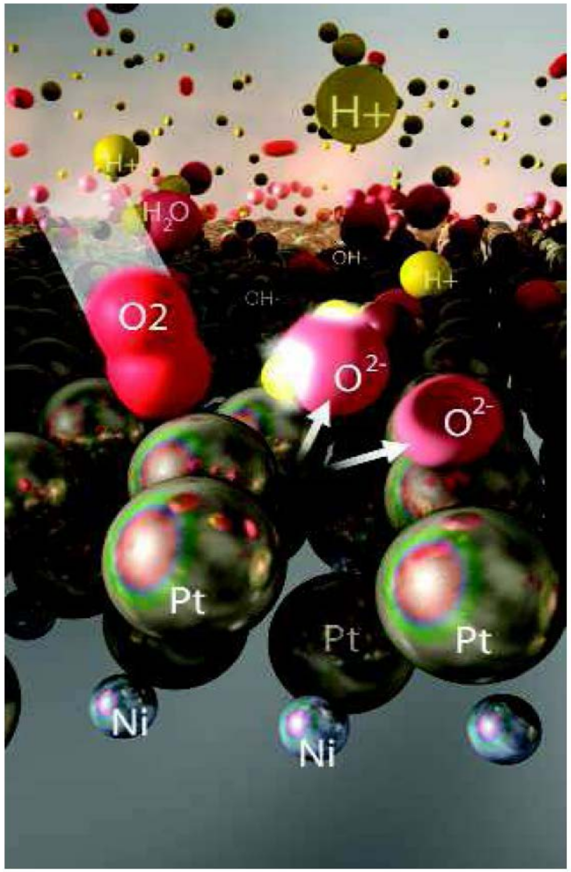




**$Pt_3Ni(111)$/Pt-Skin Surface is the most active catalyst for the ORR (100-fold enhancement)**

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



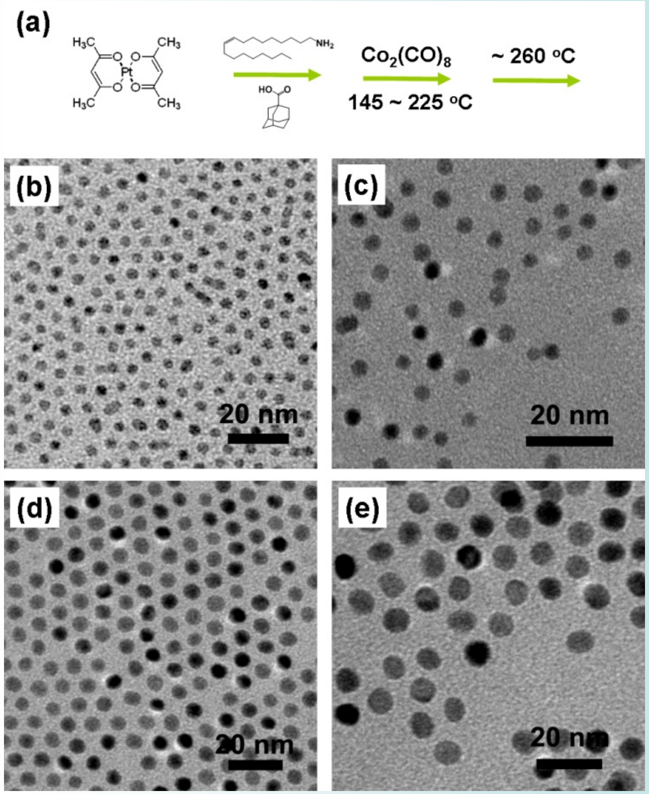






$Pt_3Ni(111)$/Pt-Skin Surface is the most active catalyst for the ORR (100-fold enhancement)

# Controlled Synthesis: *Multimetallic Nanocatalysts*

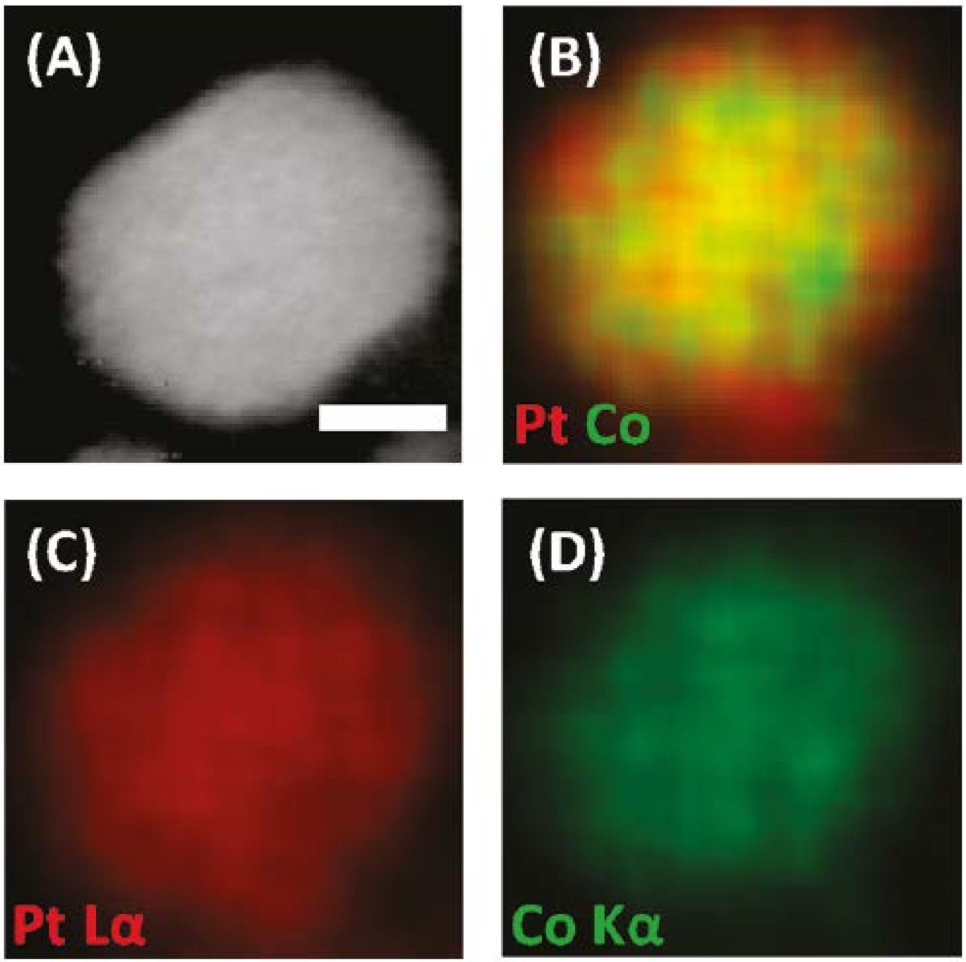
**Colloidal solvo - thermal approach has been developed for monodispersed PtM NPs with controlled size and composition**



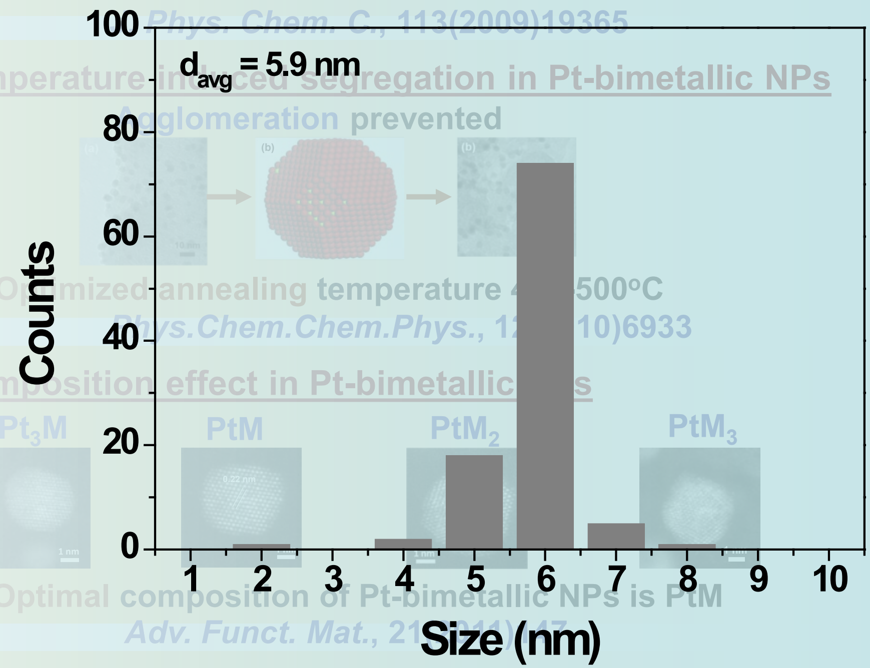

**Efficient surfactant removal method does not change the catalyst properties**

# PtM Alloy NPs | Distribution: *Elements and Particle Size*

## HAADF - STEM

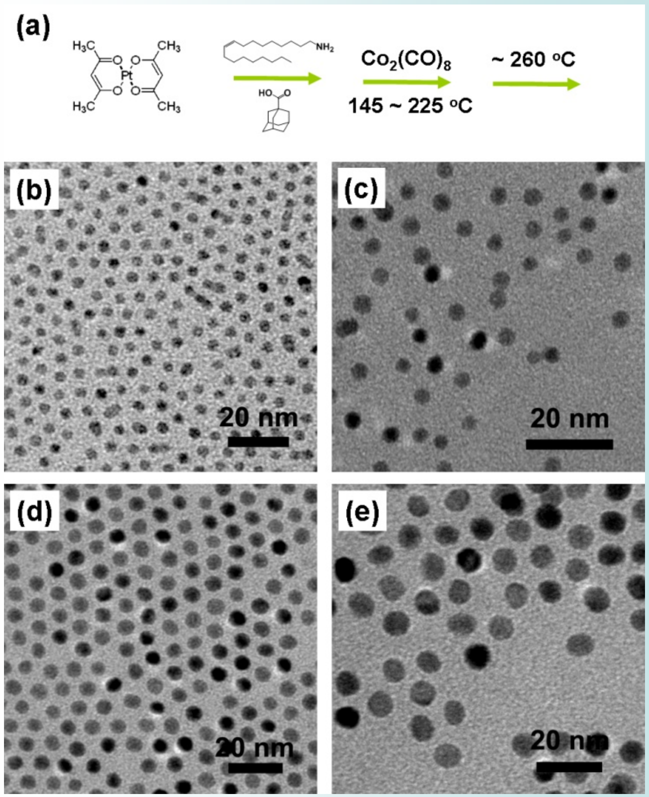



## Particle size distribution



# Controlled Synthesis: *Multimetallic Nanocatalysts*

**Colloidal solvo - thermal approach** has been developed for monodispersed PtM NPs with **controlled size and composition**




**Efficient surfactant removal** method does not change the catalyst properties

## 1° Particle size effect applies to Pt-bimetallic NPs

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

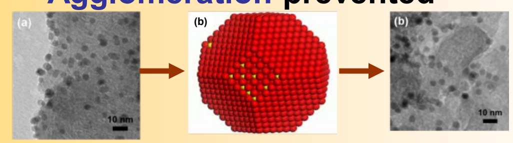
**Mass Activity** decreases with particle size

**Optimal size particle size** ~5nm

*J. Phys. Chem. C.*, 113(2009)19365

## 2° Temperature induced segregation in Pt-bimetallic NPs

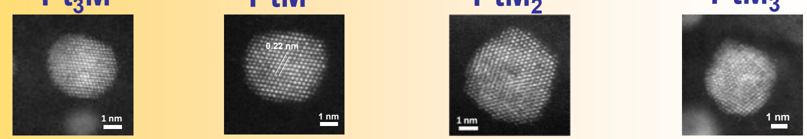
**Agglomeration** prevented




**Optimized annealing** temperature 400-500°C

*Phys.Chem.Chem.Phys.*, 12(2010)6933

## 3° Composition effect in Pt-bimetallic NPs

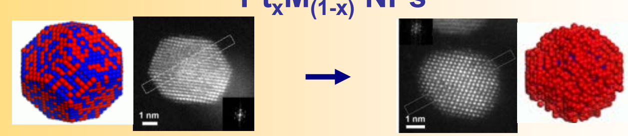



**Optimal** composition of Pt-bimetallic NPs is PtM

*Adv. Funct. Mat.*, 21(2011)147

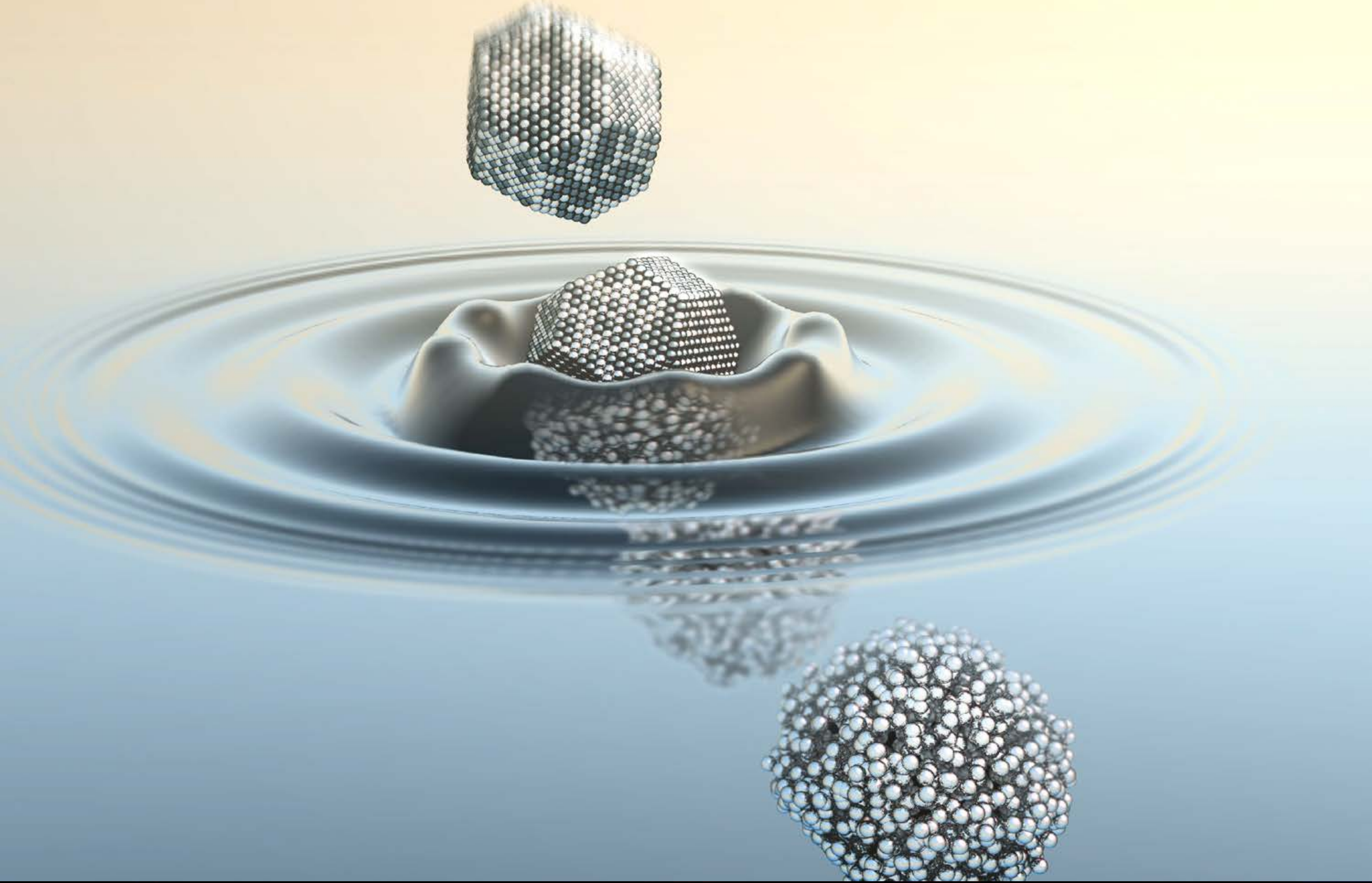
## 4° Surface chemistry of homogeneous Pt-bimetallic NPs

$Pt_xM_{(1-x)}$ NPs

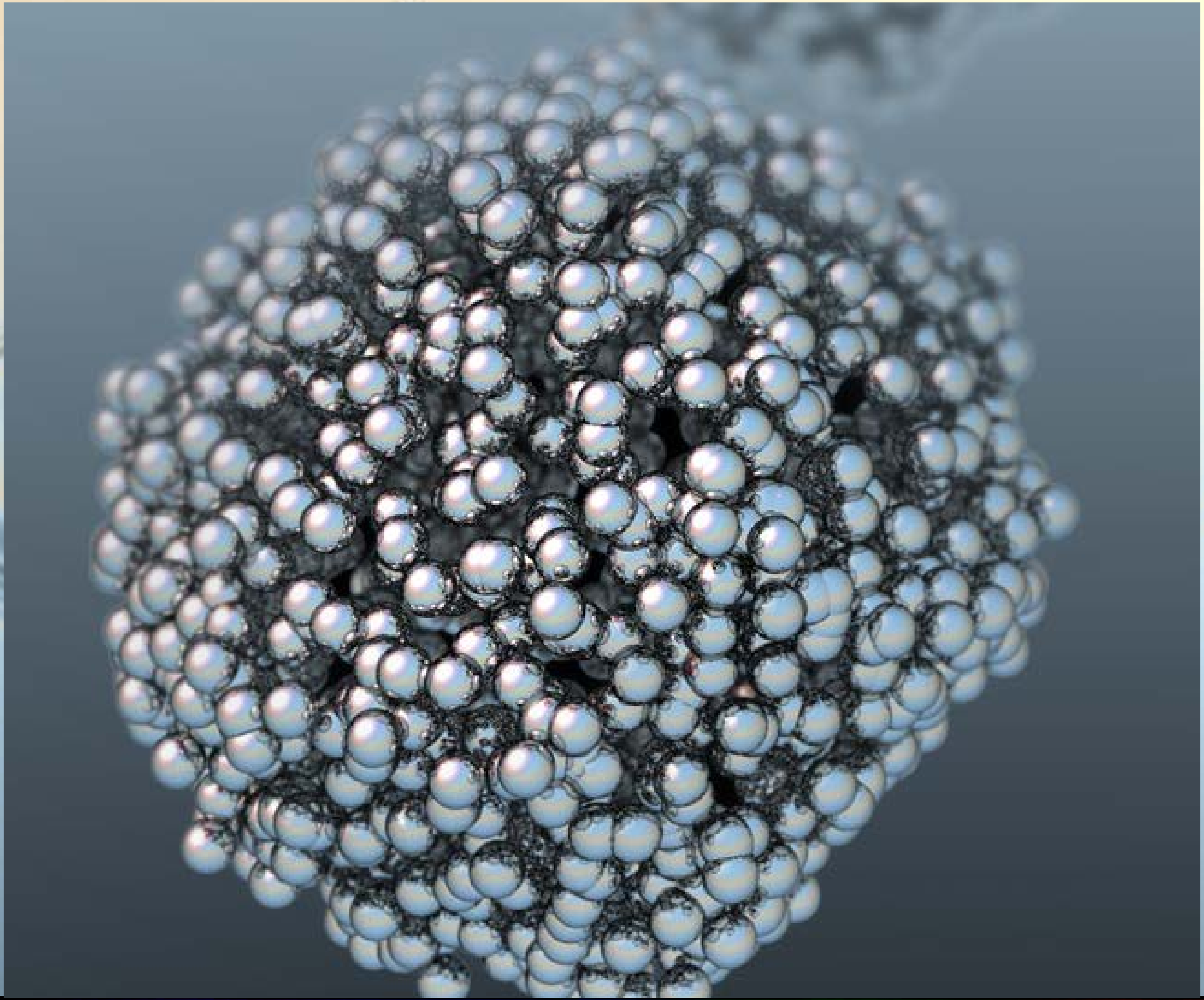



**Dissolution** of non Pt atoms forms **Pt-skeleton** surface

# $Pt_xNi_{1-x}$: *Surface Chemistry and Composition Effect*

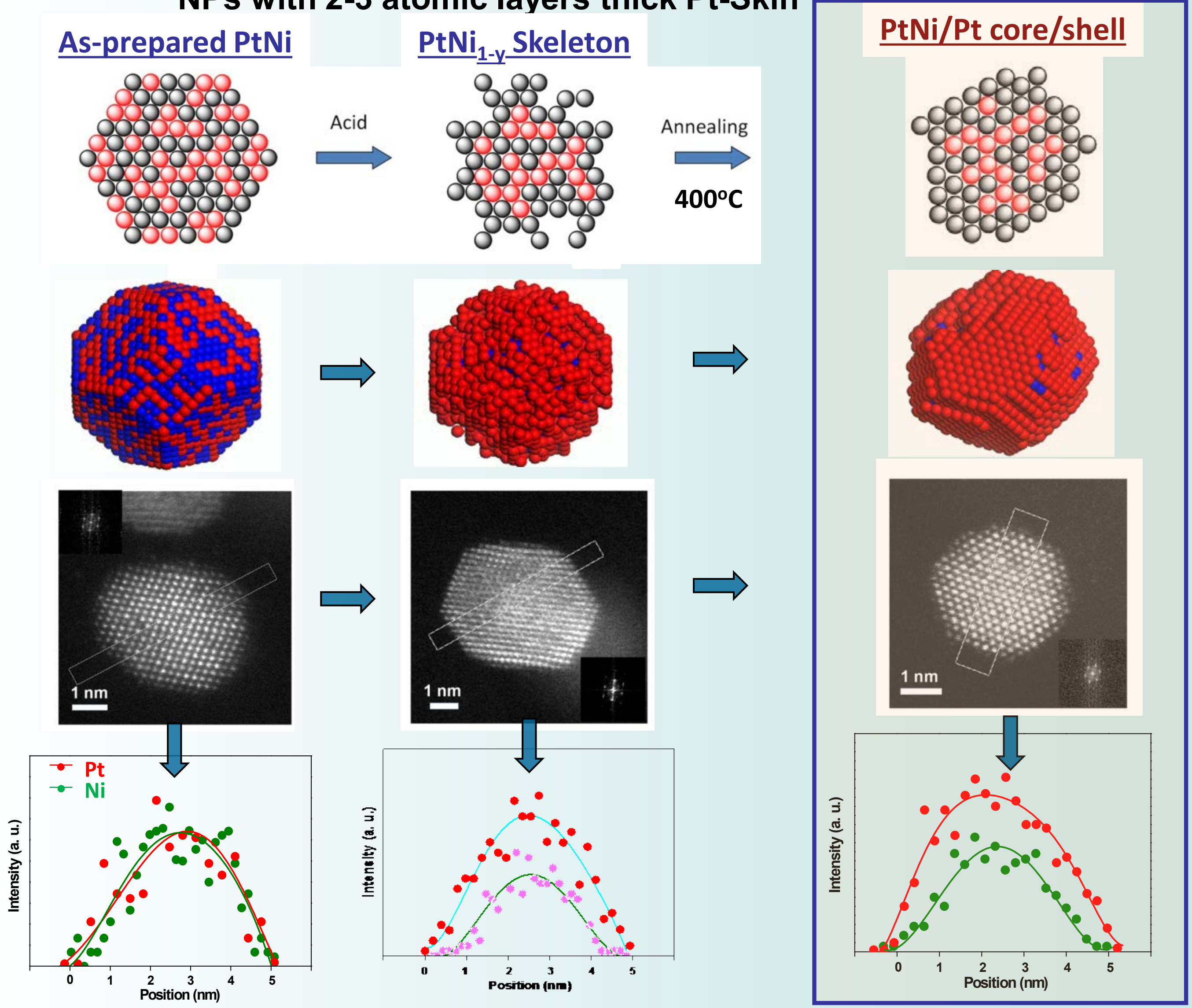


# $Pt_xNi_{1-x}$: *Surface Chemistry and Composition Effect*



# PtNi with multilayered Pt-Skin Surfaces : *Tailoring Nanoscale Surfaces*

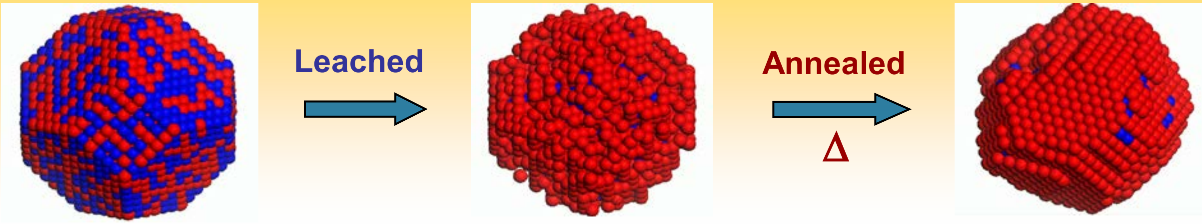
**Temperature annealing protocol** used to transform $PtNi_{1-x}$ skeletons to multilayered PtNi/Pt NPs with 2-3 atomic layers thick Pt-Skin

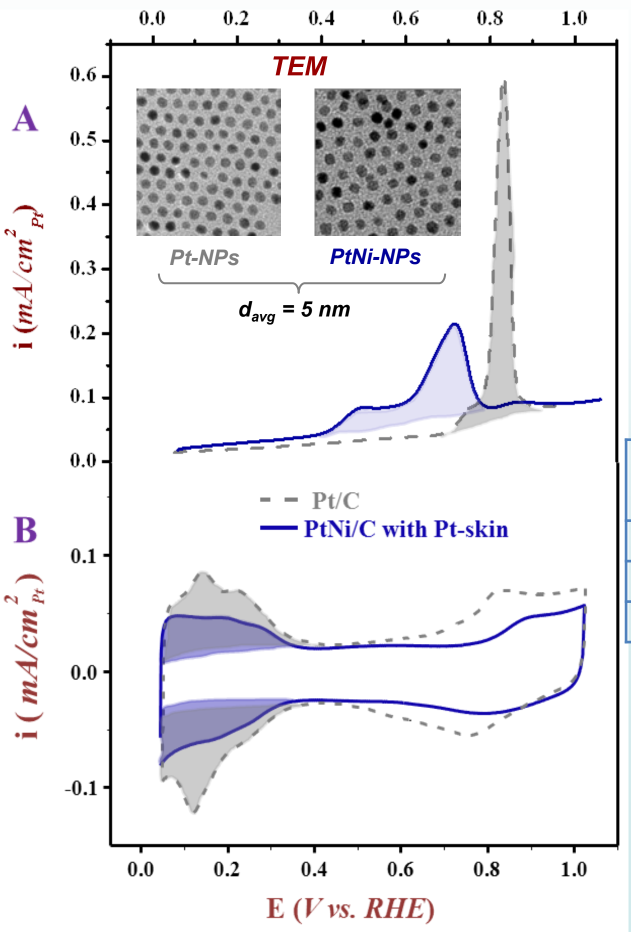



**HRTEM**

**Line profile**

# NPs with multilayered 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)

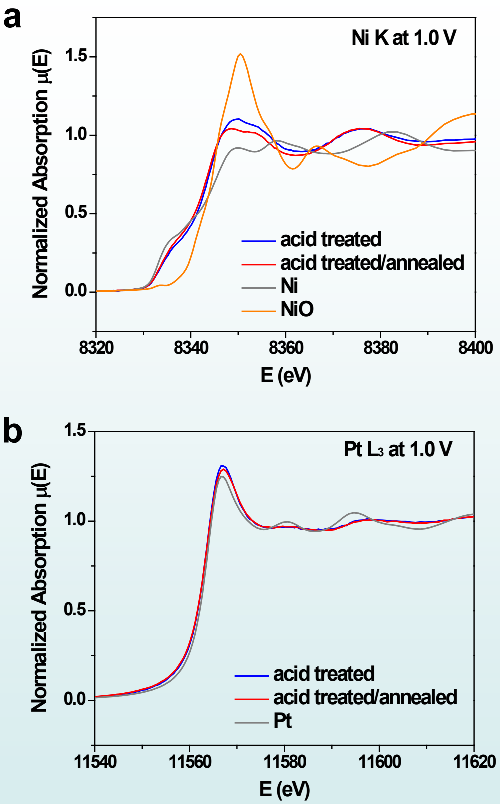
**Surface coverage of adsorbed CO is not affected on Pt-skin surfaces**

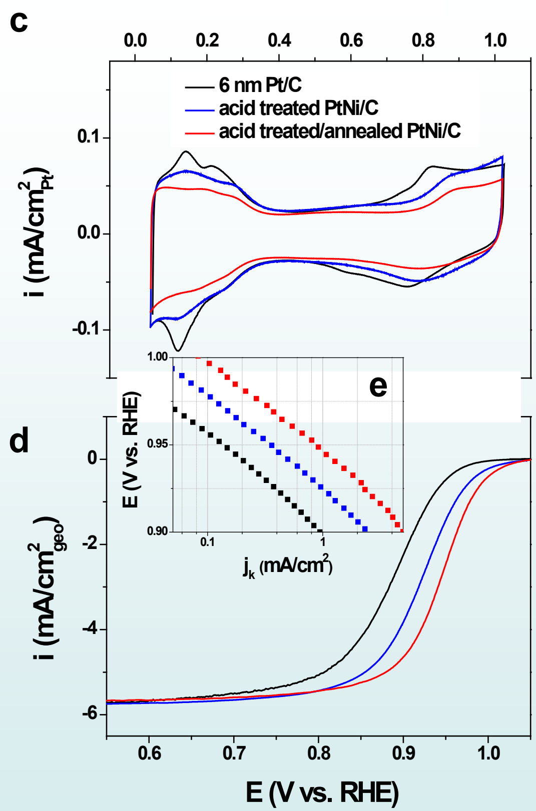
**Ratio between $Q_{CO}/Q_{Hupd}$>1 is indication of Pt-skin formation**

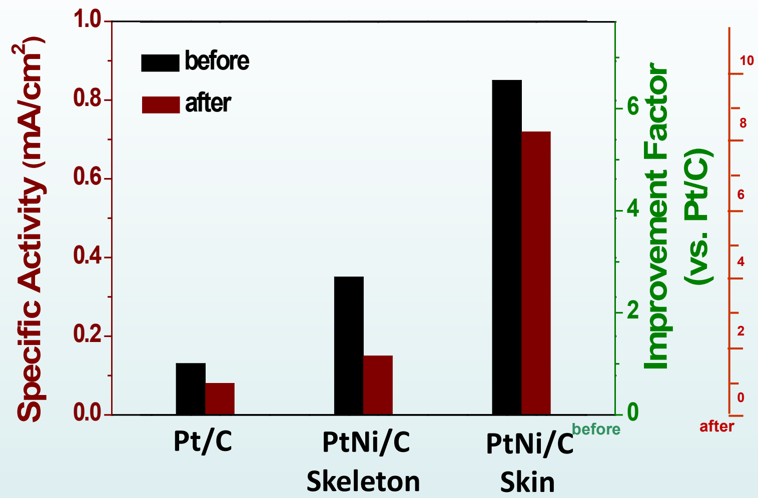
| Catalyst | $Q_H$ (μC) | $ECSA_H$ (cm²) | $Q_{CO}$ (μC) | $ECSA_{CO}$ (cm²) | $Q_{CO}/2Q_H$ |
|---|---|---|---|---|---|
| Pt/C | 279 | 1.47 | 545 | 1.41 | 0.98 |
| PtNi/C | 292 | 1.54 | 615 | 1.60 | 1.05 |
| PtNi-skin/C | 210 | 1.10 | 595 | 1.54 | 1.42 |

**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*




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

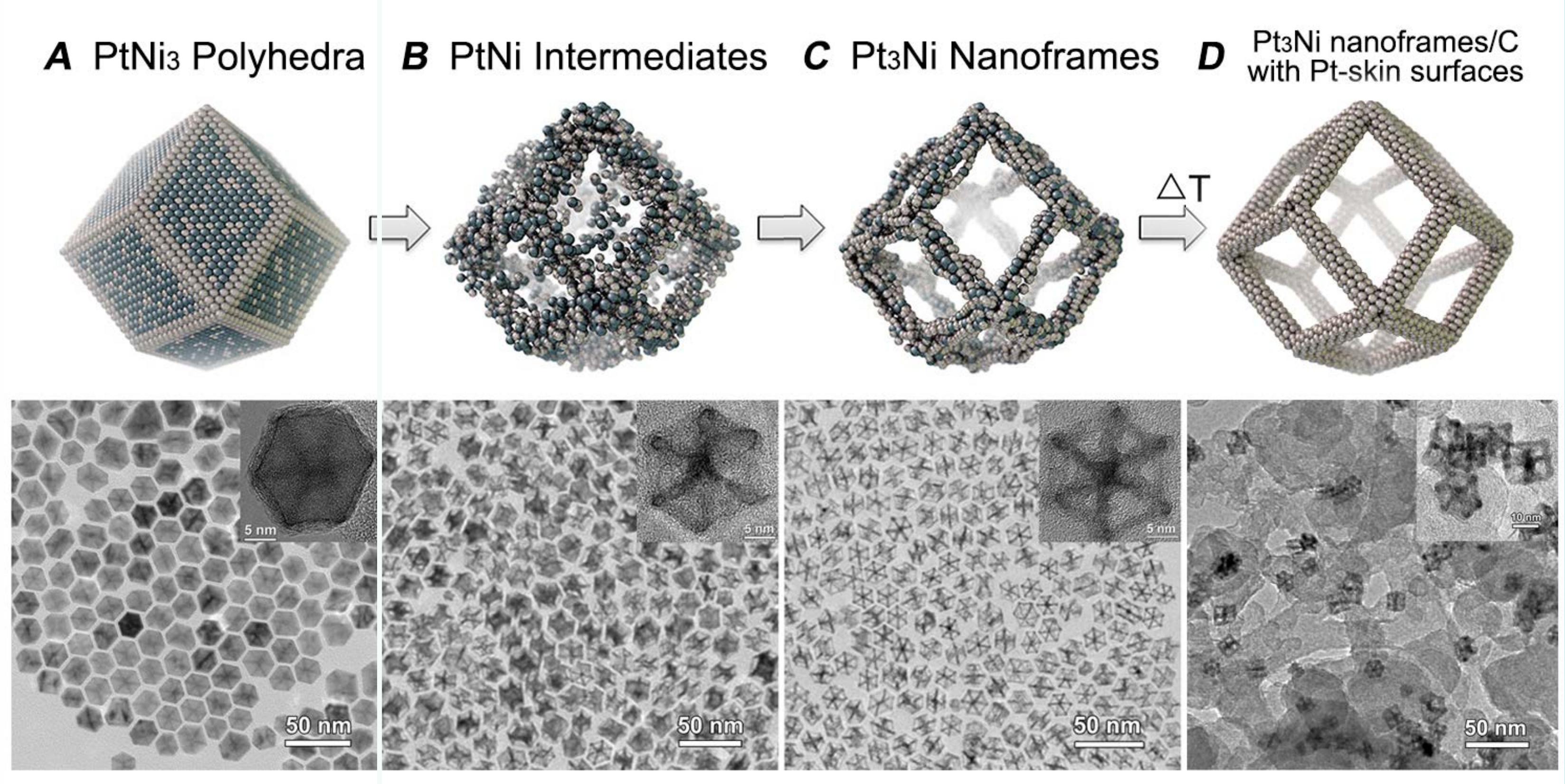
**RDE:** PtNi-Skin catalyst exhibits superior catalytic performance for the ORR and is highly durable system

***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

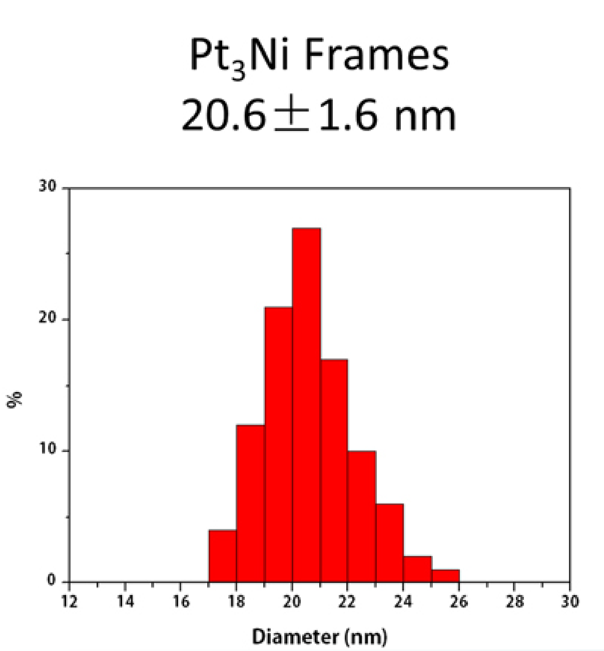
# Mass Activity Enhancement by 3D Surfaces: *Multimetallic Nanoframes*

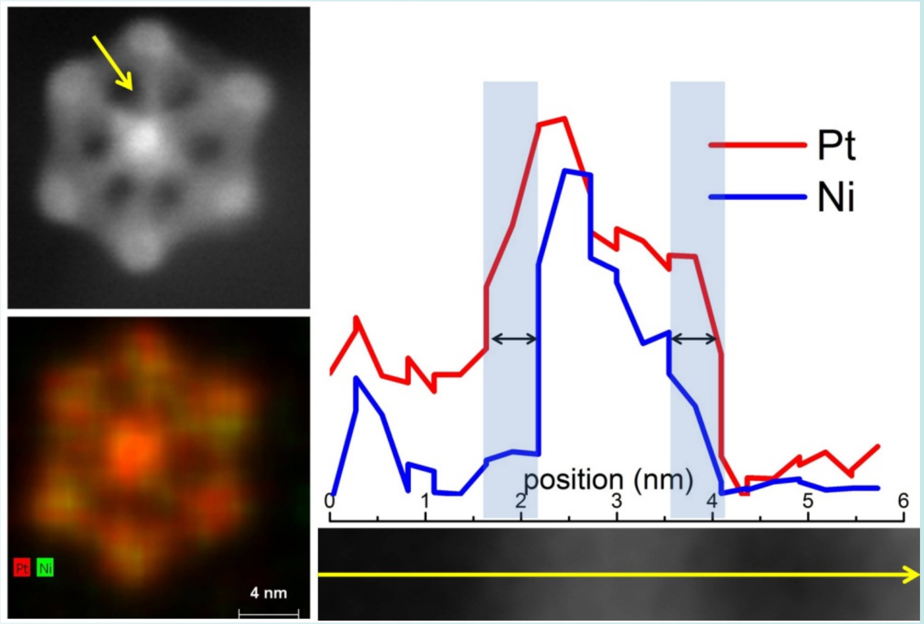
**In collaboration with Peidong Yang, UC Berkeley**




- $H_2PtCl_6$ and $Ni(NO_3)_2$ react in oleylamine at 270°C for 3 min forming solid $PtNi_3$ polyhedral NPs
- Reacting solution is exposed to $O_2$ that induces spontaneous corrosion of Ni
- Ni rich NPs are converted into $Pt_3Ni$ nanoframes with Pt-skeleton type of surfaces
- Controlled annealing induces Pt-Skin formation on nanoframe surfaces

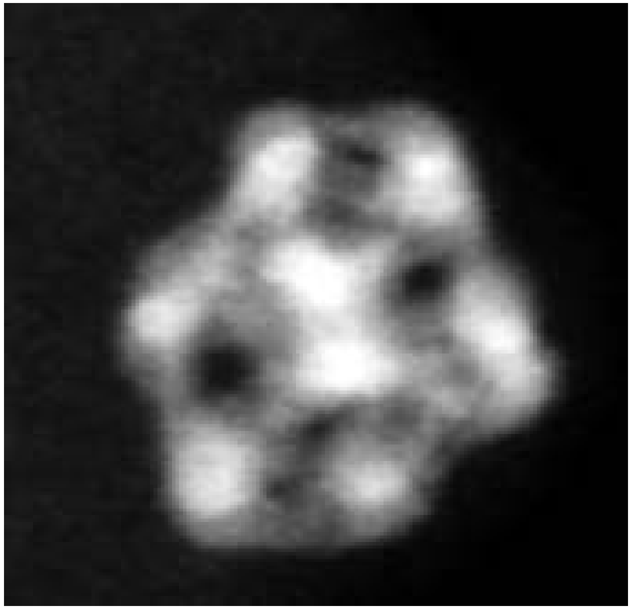
# Compositional Profile: *PtNi Nanoframes with Pt-skin Surfaces*

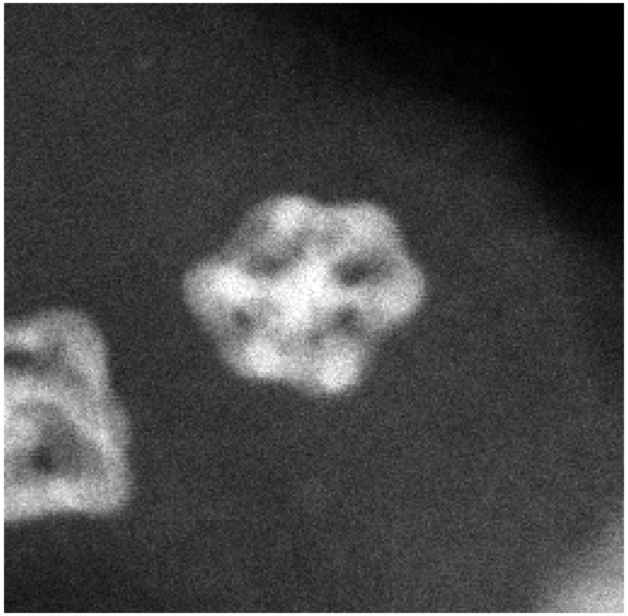


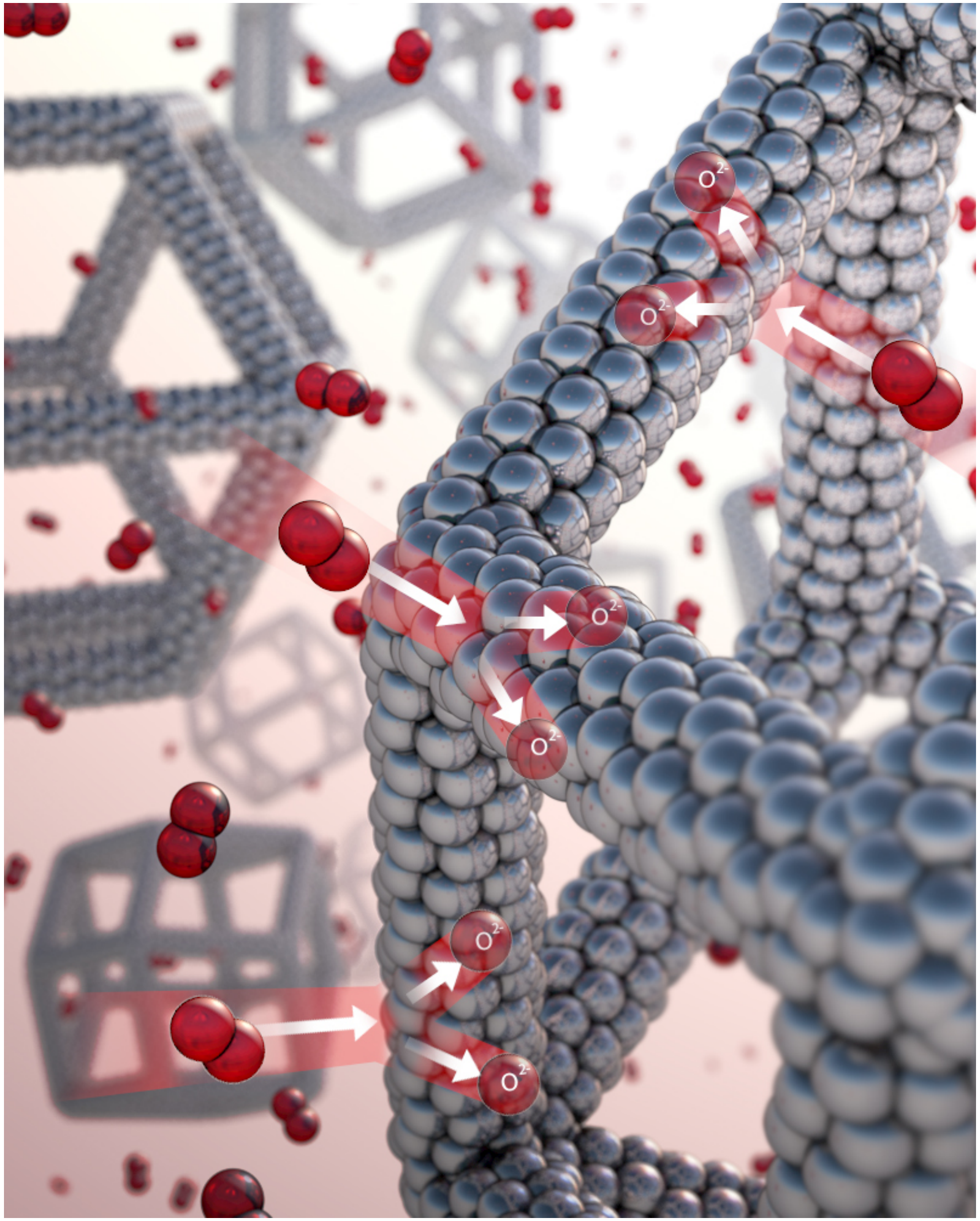




- Narrow particle size distribution
- Hollow interior
- Formation of Pt-skin with the thickness of 2ML
- Surfaces with 3D accessibility for reactants
- Segregated compositional profile  with overall $Pt_3Ni$ composition

# *Multimetallic Nanoframes with 3D Electrocatalytic Surfaces*

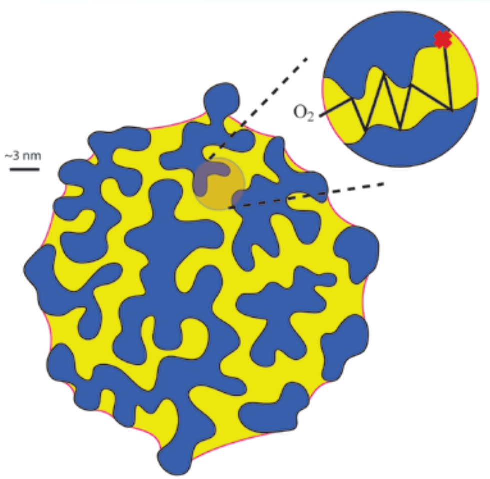






# Improving the ORR Rate by *Protic Ionic Liquids*

[MTBD][beti]

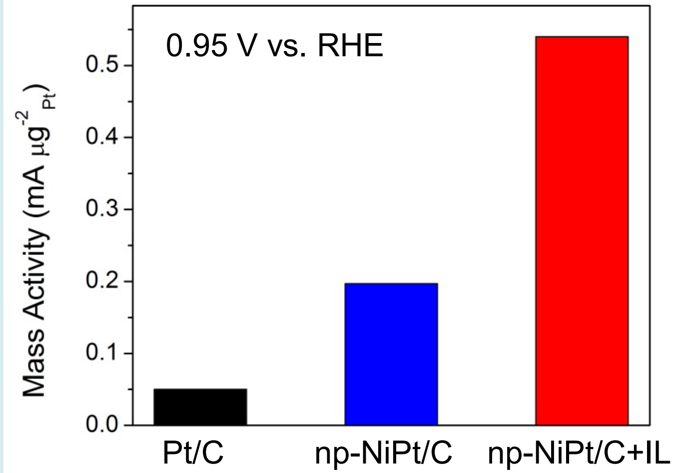


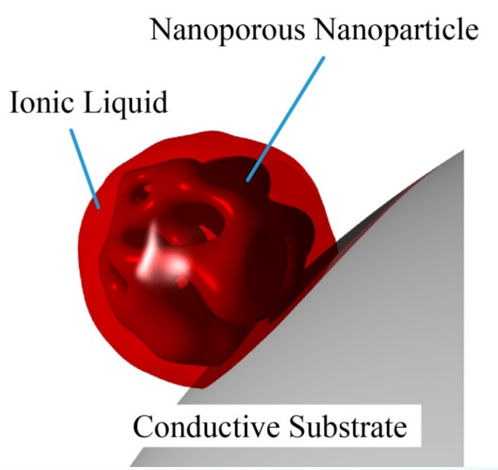

**Chemically Tailored Interface**

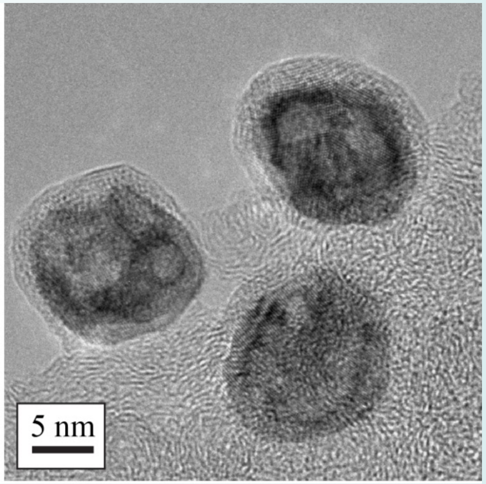
High $O_2$ solubility along with hydrophobicity yield improved ORR kinetics

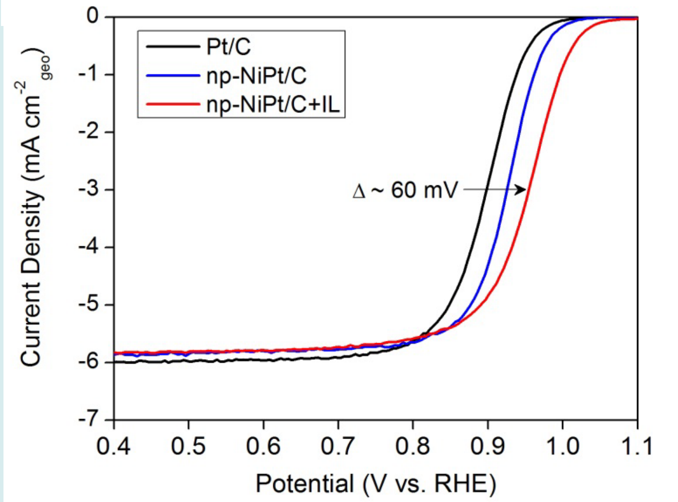
- Higher $O_2$ solubility than $H_2O$
- Protic (high proton conductivity)
- Hydrophobic
- Thermally Stable

$$\frac{C_{O_2,[\mathrm{MTBD}][beti]}}{C_{\mathrm{O_2,HClO_4}}} = 2.40 \pm 0.013$$

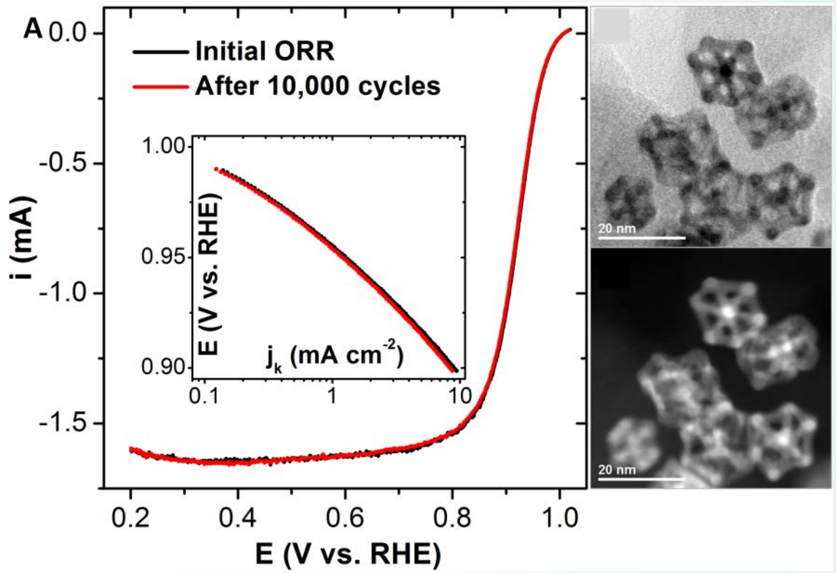


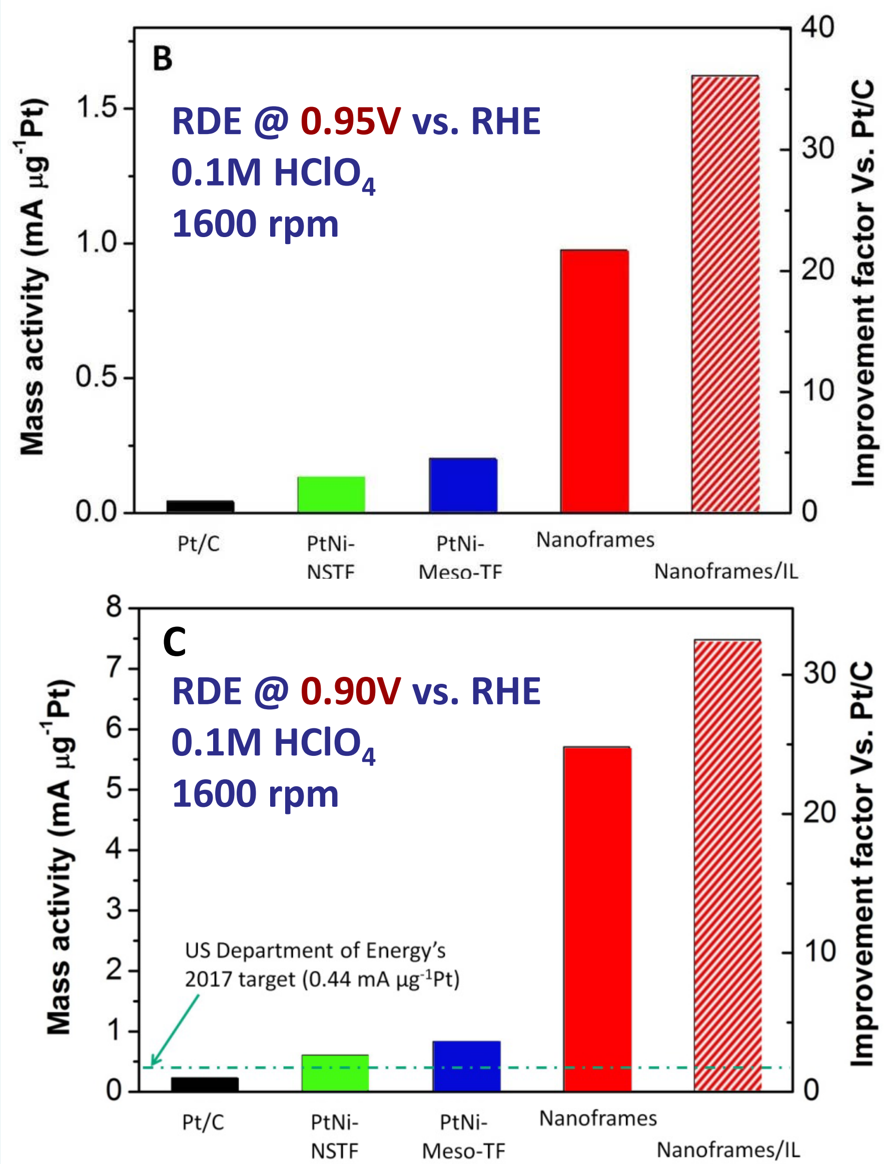



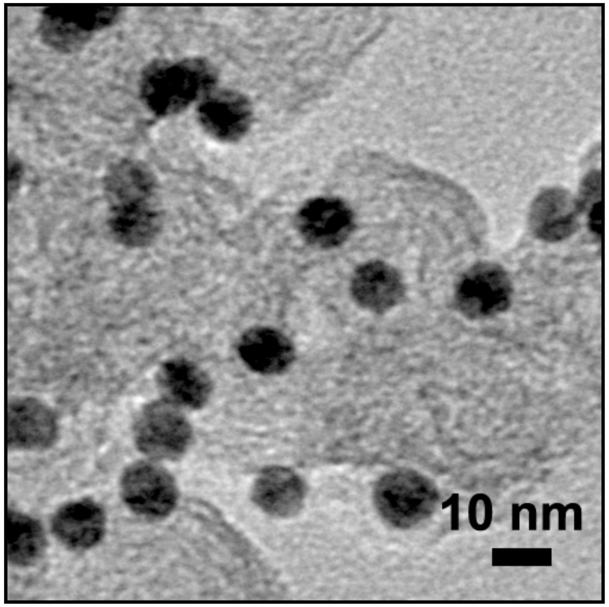
# Tailoring Activity: *PtNi Nanoframes as the ORR Electrocatalyst*

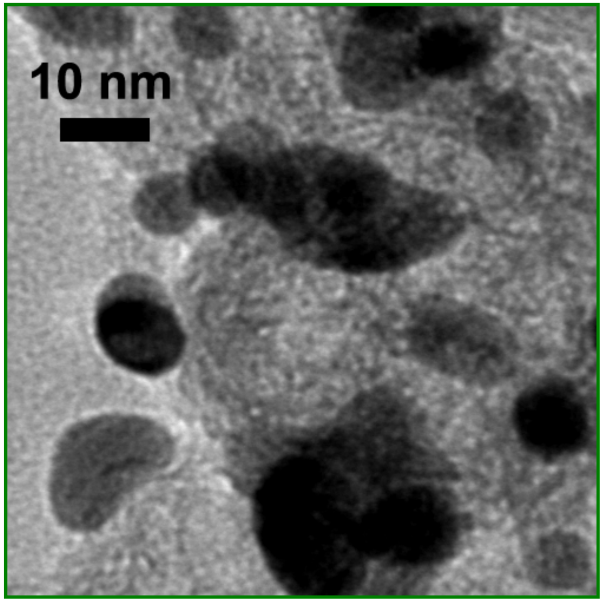



- No change in activity after 10K cycles 0.6 – 1.0 V
- Specific activity increase over 20-fold vs. Pt/C
- Mass activity increase over 35-fold vs. Pt/C
- Increase in mass activity over 15-fold vs. DOE target



## DURABILITY: *Pt/C*



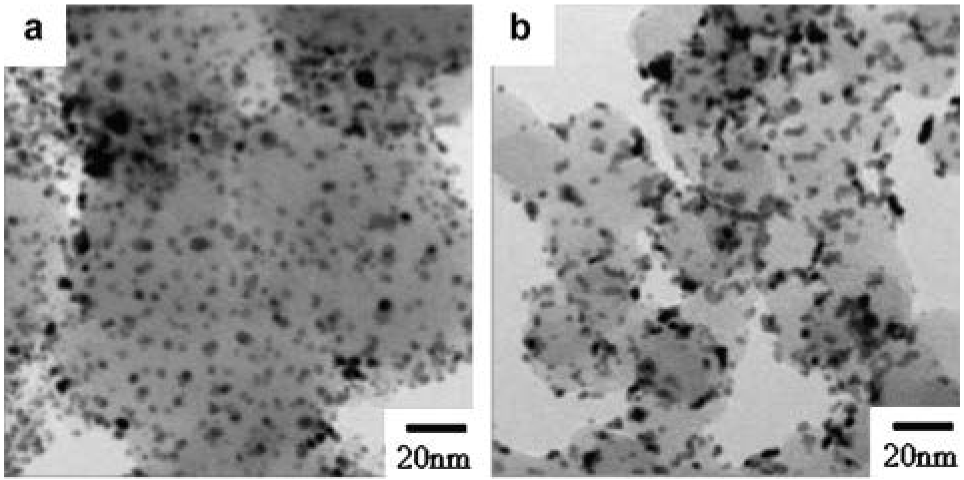




**Initial morphology**

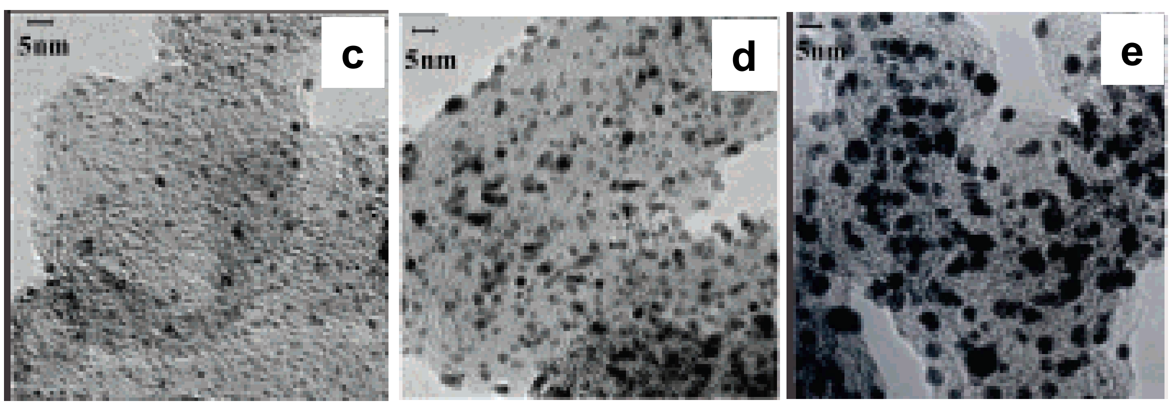
**After 60,000 cycles**

**Potential Range: 0.6-1.0V**

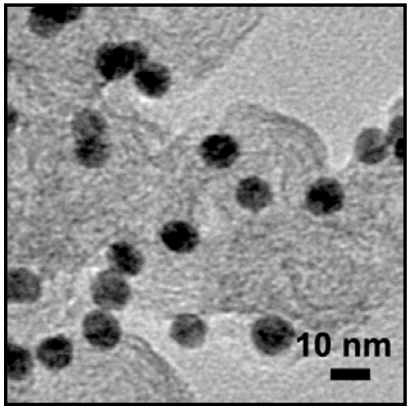
# Commercial *Pt/C* Catalysts




- Commercial catalysts are usually made by impregnation methods.
- Poor control
  - Broad size distribution
  - Different, undefined morphologies, but everyone calls them "cubo-octahedral", which is, in fact, not correct!

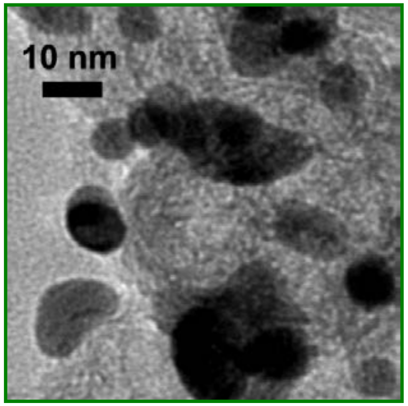


# DURABILITY: *Pt/C*



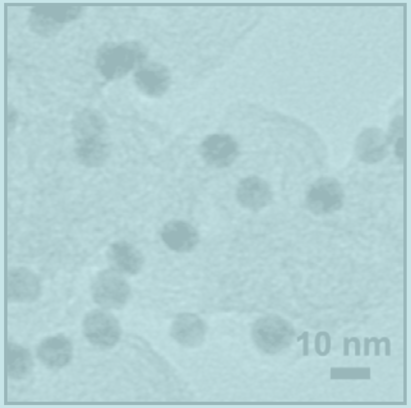

Initial morphology

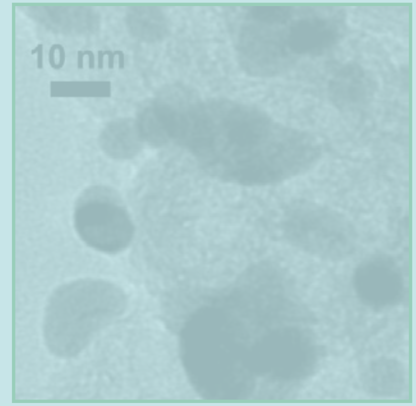
Potential Range: 0.6-1.0V




After 60,000 cycles

# DURABILITY: *Pt/C*

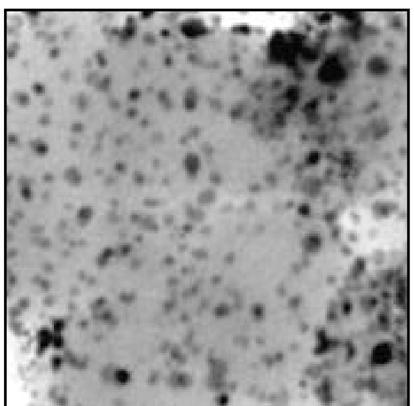


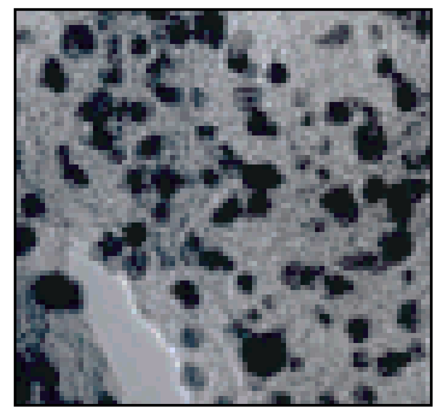




**Initial morphology**

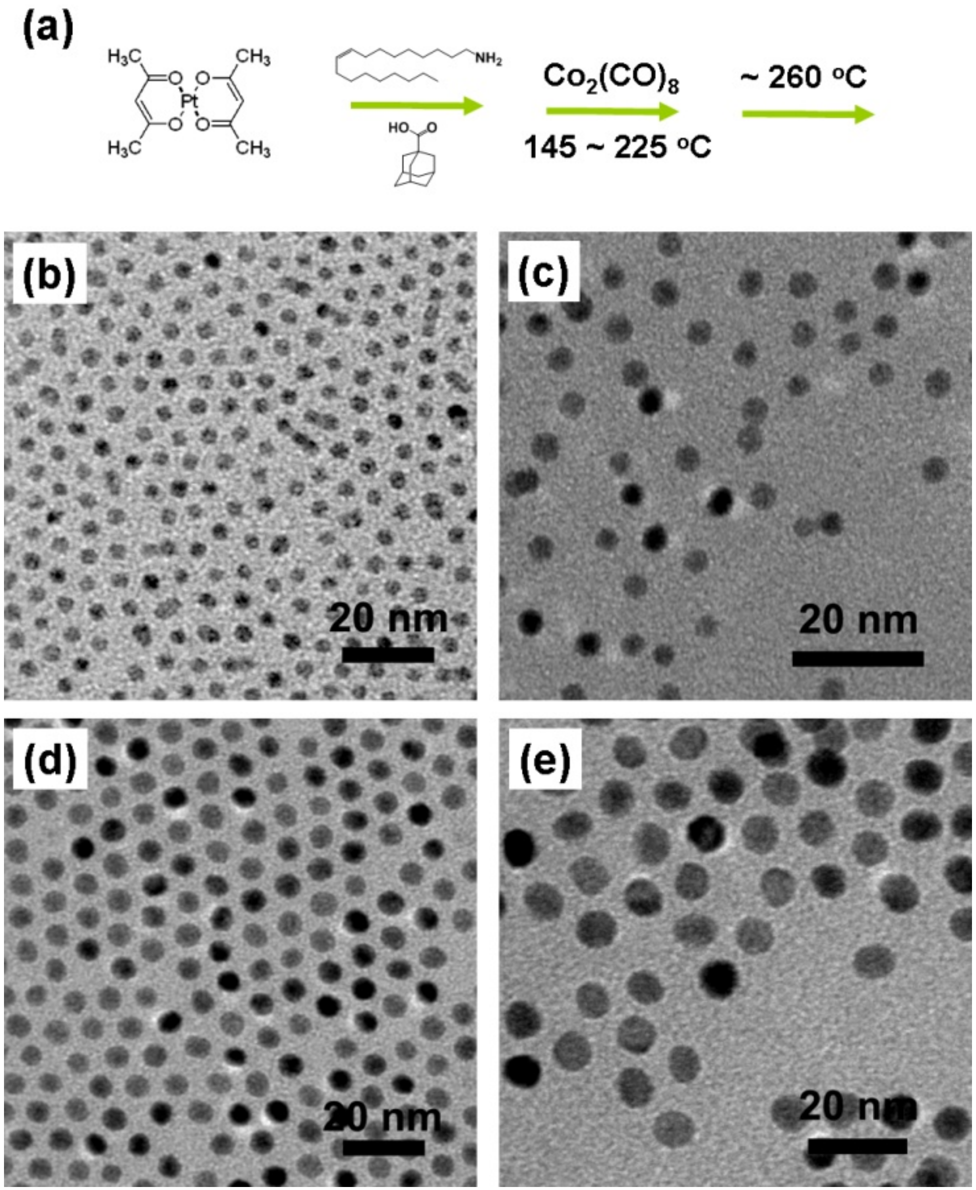
**Potential Range: 0.6-1.0V**

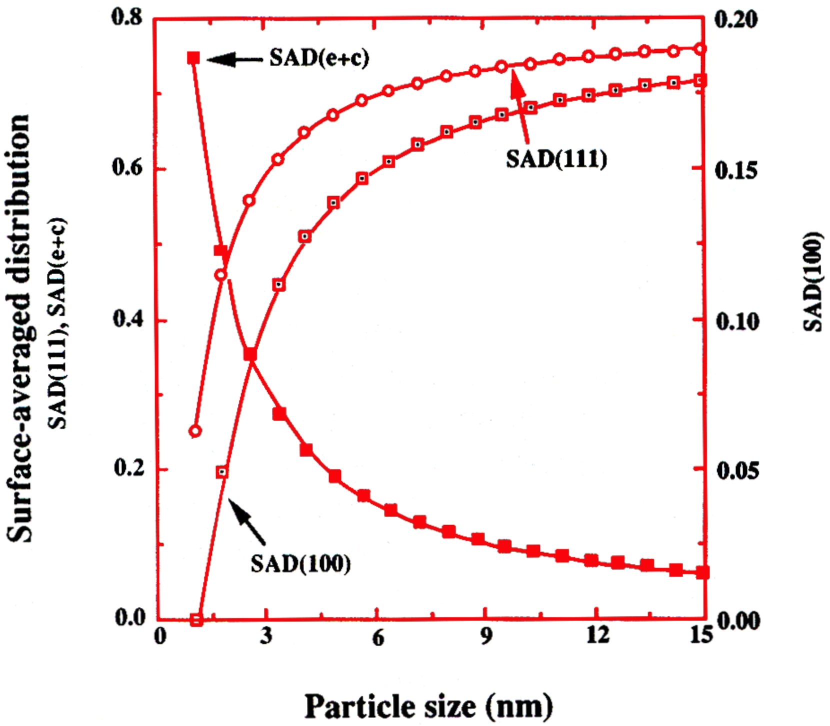
**After 60,000 cycles**



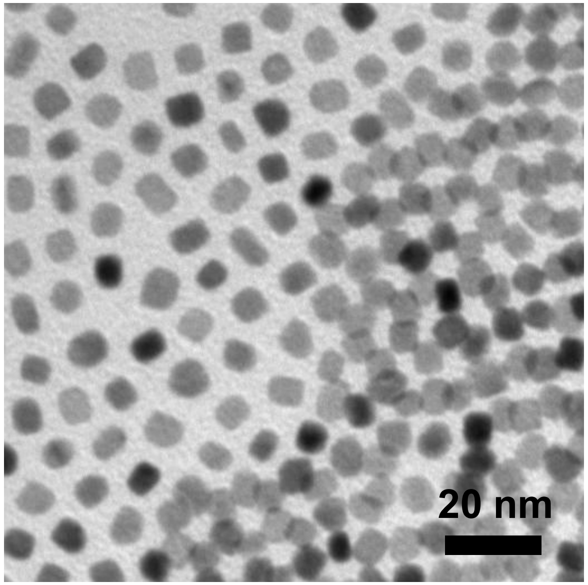


# SIZE EFFECT(s)? *Pt/C*

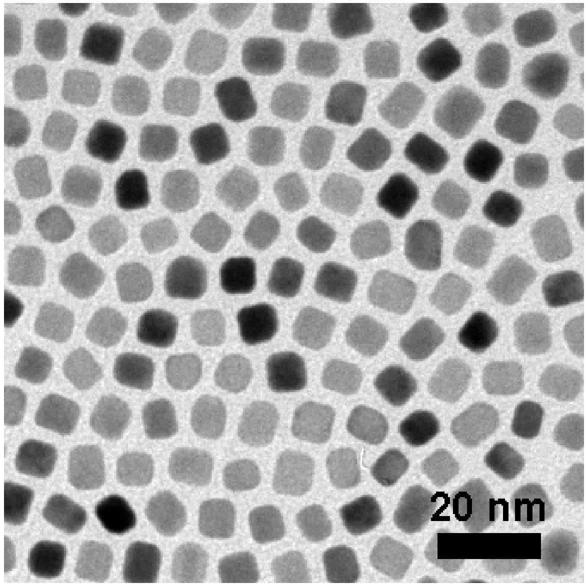


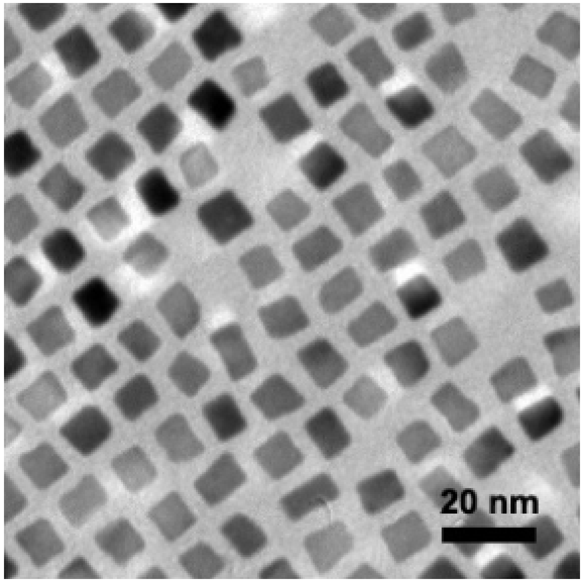
# SHAPE EFFECT(s)? *Pt/C*




cubo-octahedron




truncated cube

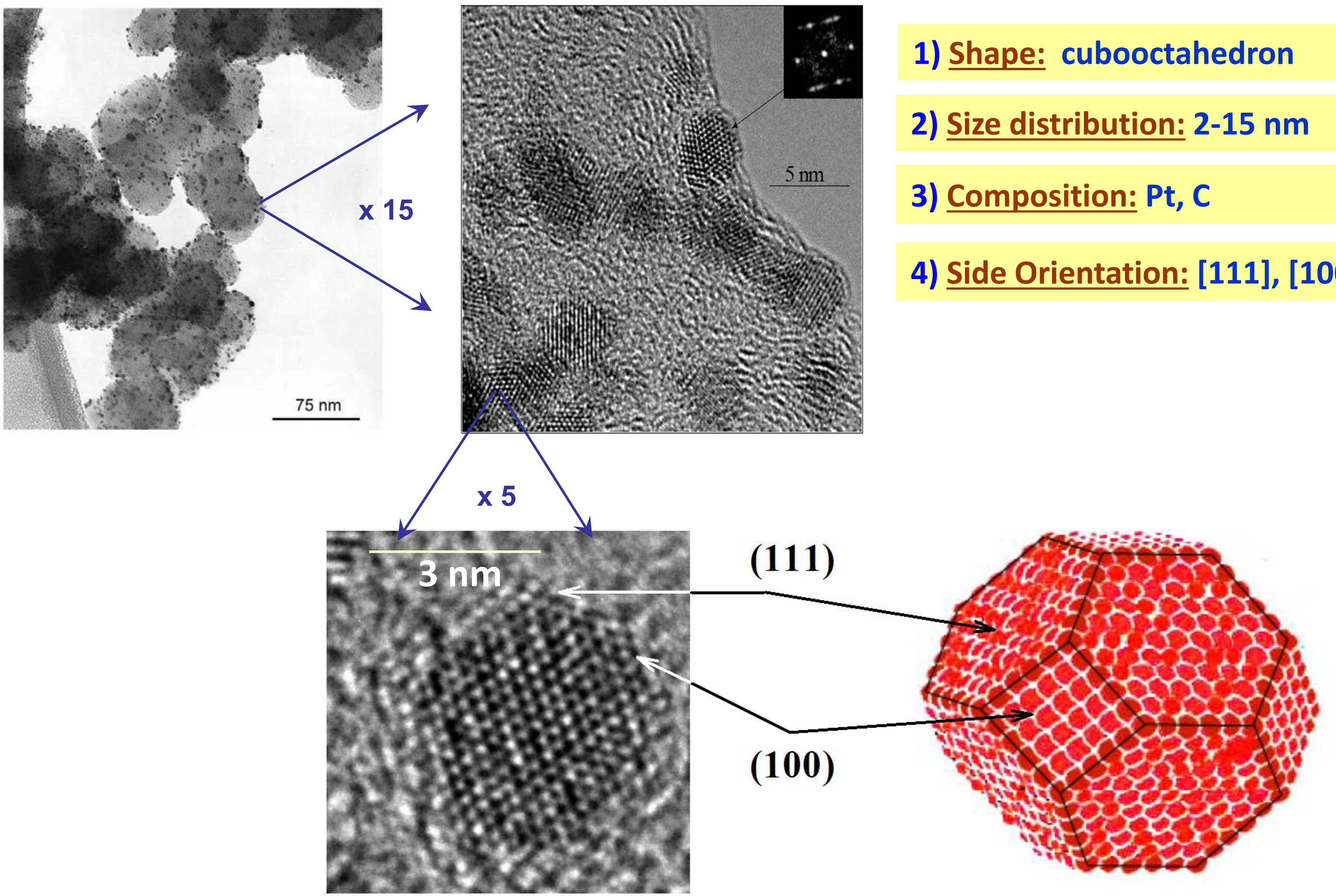



cube

- Uniform morphology
- Size control

  octahedron (?) → cubo-octahedral → Cube

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



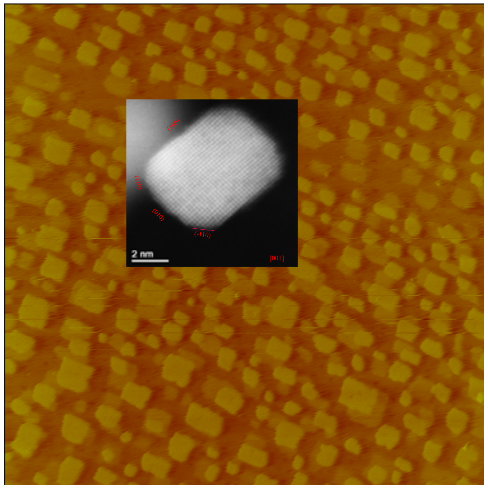

1) Shape: cubooctahedron

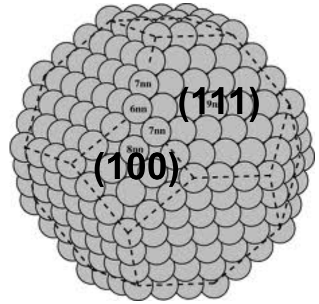
2) Size distribution: 2-15 nm

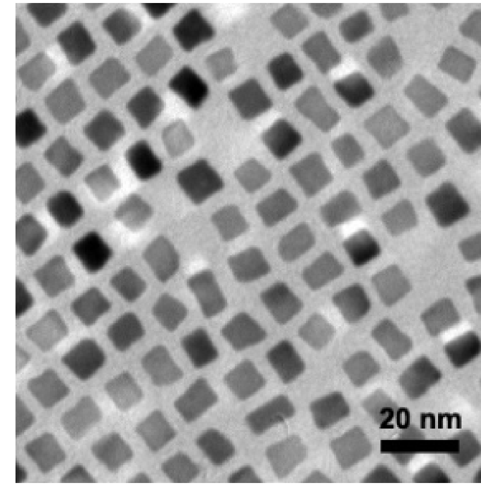
3) Composition: Pt, C

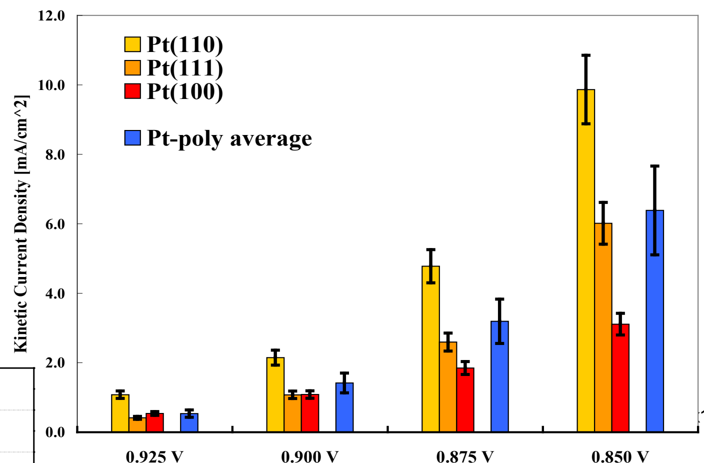
4) Side Orientation: [111], [100]

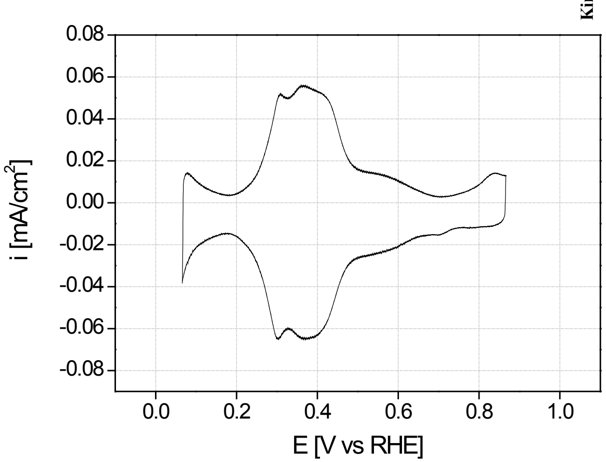
# APPROACH: *Well-Defined Systems (ext & nano)*

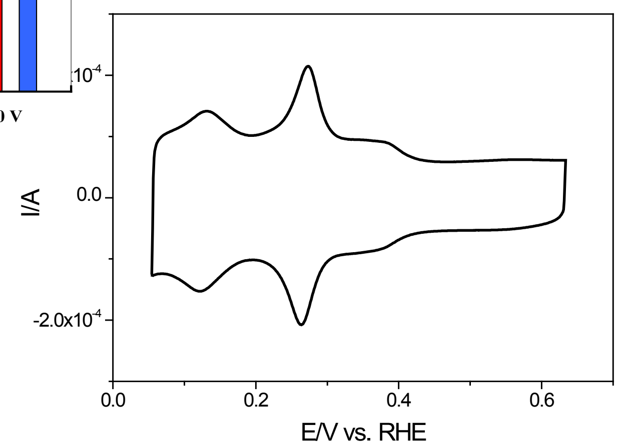


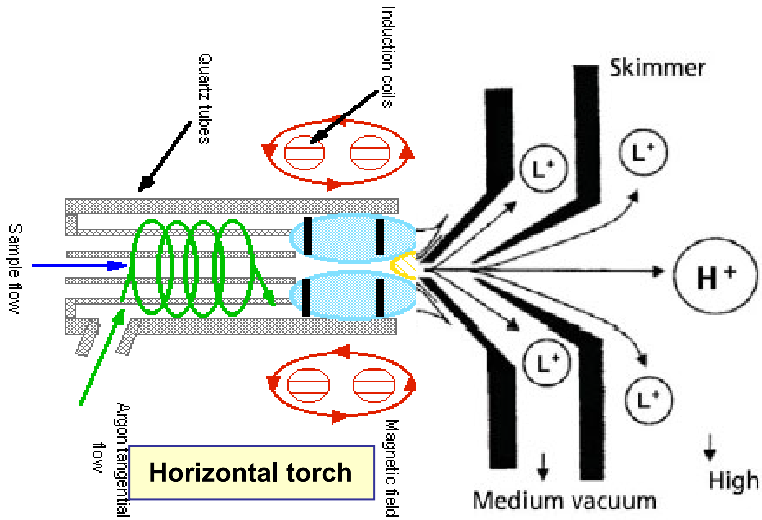



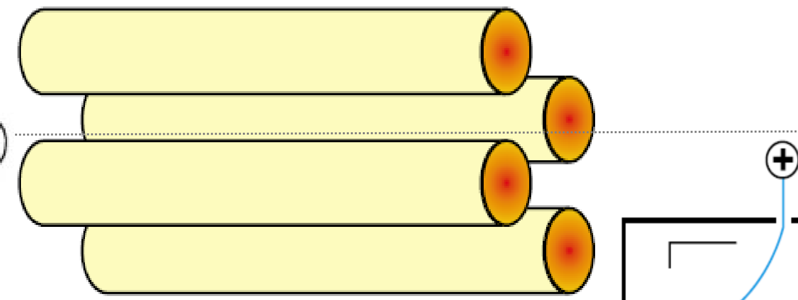



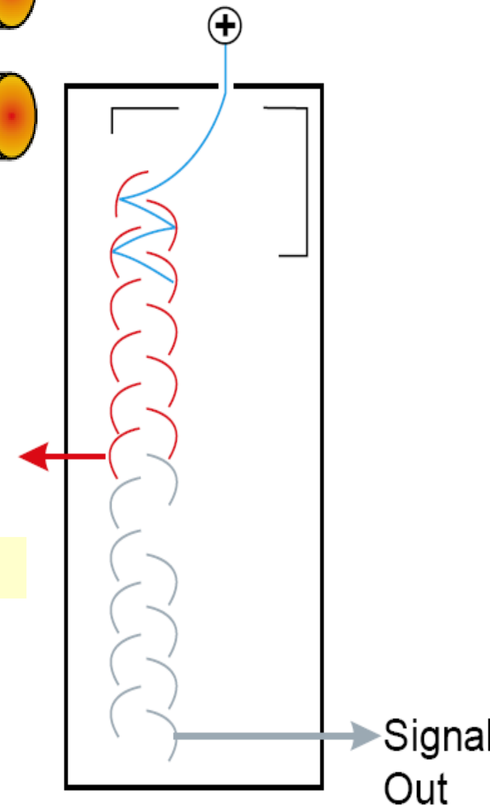



# ICP-MS: *Principle of Operation*

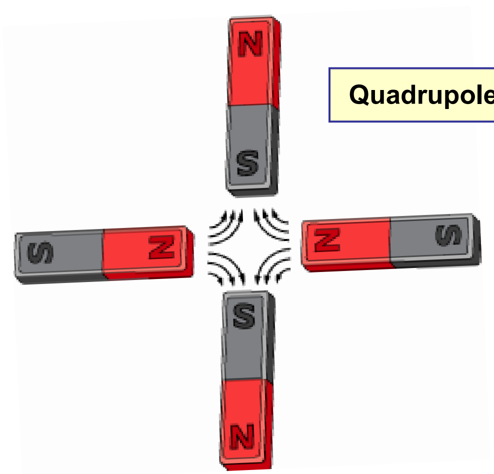



Quadrupole mass filter



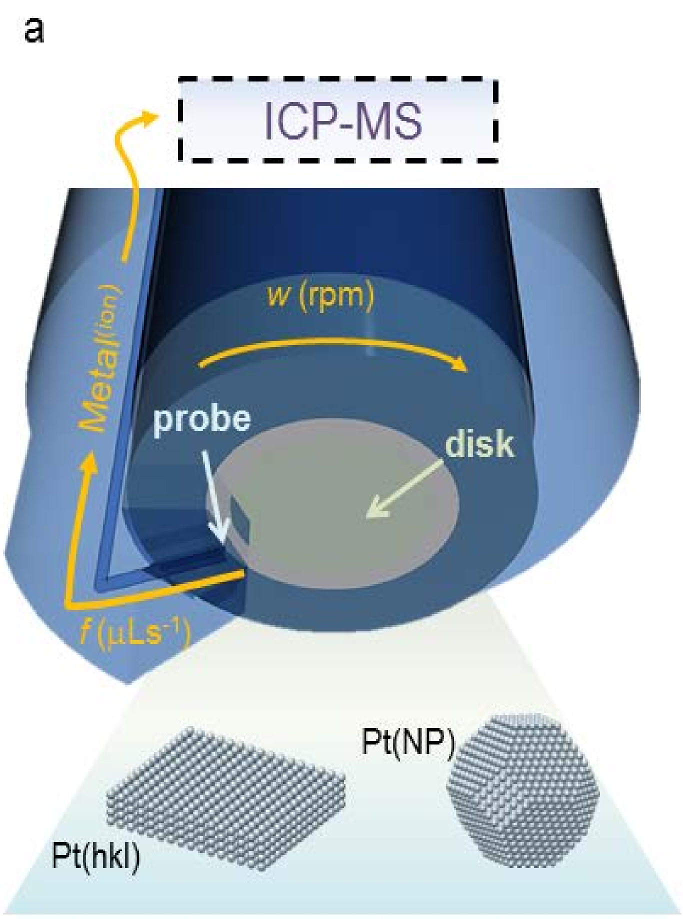



Detector

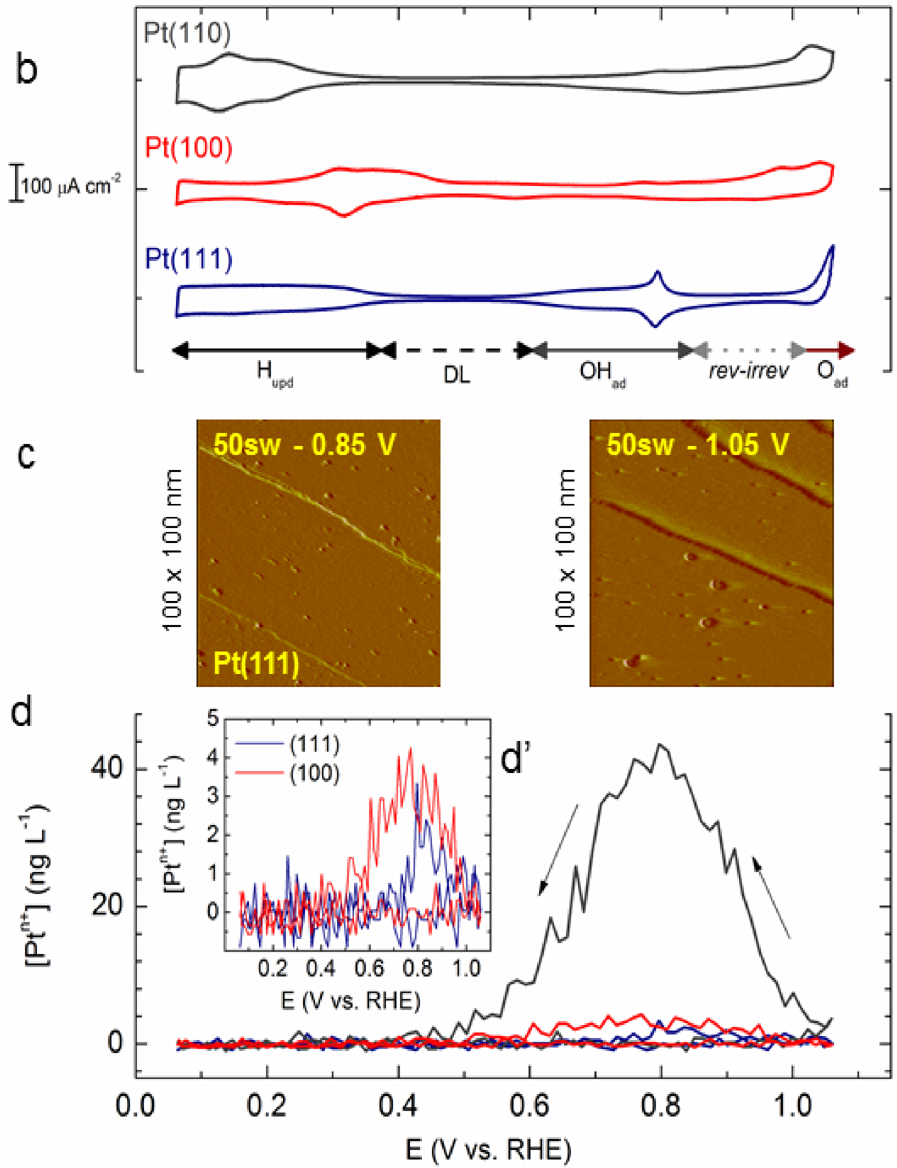



Quadrupole

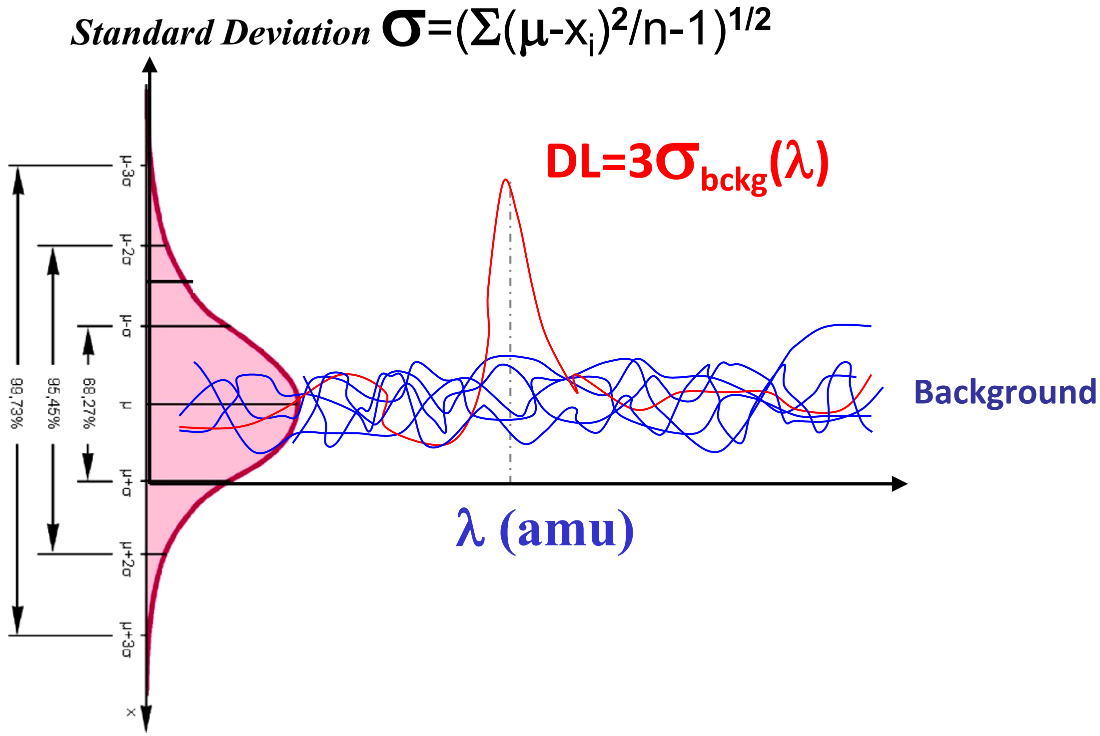
**Quadrupole allows single m/z pass at any given time**
**Time frame for the range of m/z = 1 – 240 is 0.1sec**




Rotating Disk Electrode

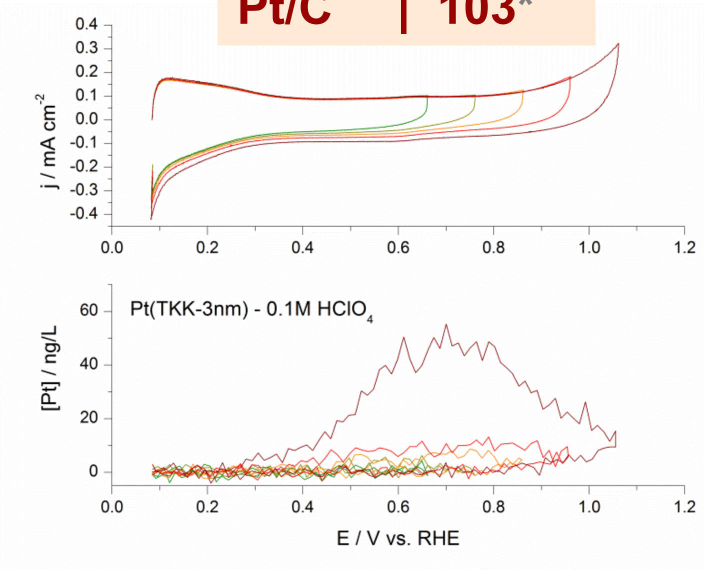


# In-Situ RDE / ICP-MS: *Pt(hkl)-Surfaces vs. Pt/C*



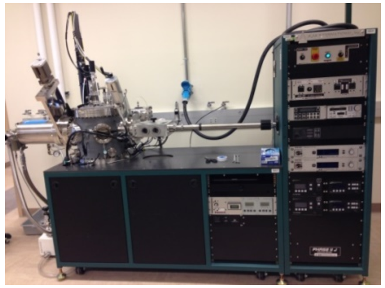

Total Pt loss over one potential cycle up to 1.05 V for distinct Pt surface morphologies, indicating the stability trend follows the coordination number of the surface sites

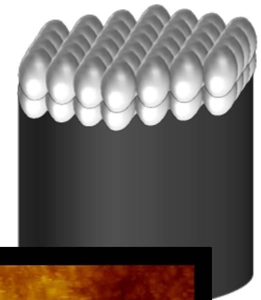
| Pt Surface | Dissolved Pt per cycle [μML] |
|---|---|
| Pt(111) | 2 |
| Pt(100) | 7 |
| Pt(110) | 83 |
| Pt-poly | 36 |
| Pt/C | 103* |



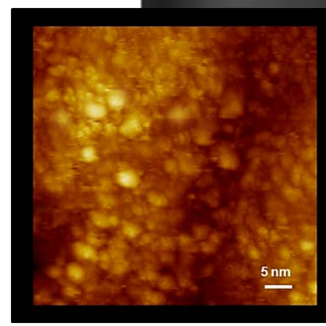

- Method detection limit (DL) is applied to blank sample prepared with all analytical steps related to given methodology, since each step is potential error source
- Limit of quantification (LOQ) is 3 times DL

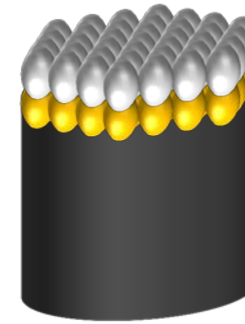
# In-Situ RDE / ICP-MS: *Pt/C, Pt and Pt/Au Well-Defined Surfaces*





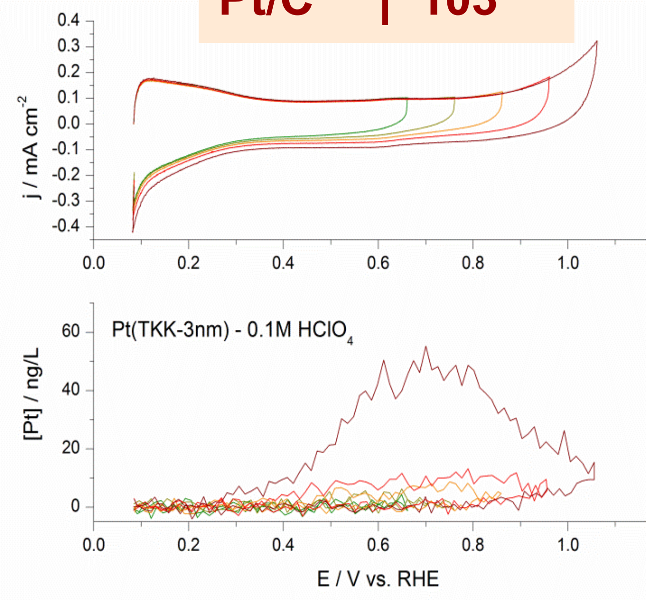
GC-Pt(4ML)

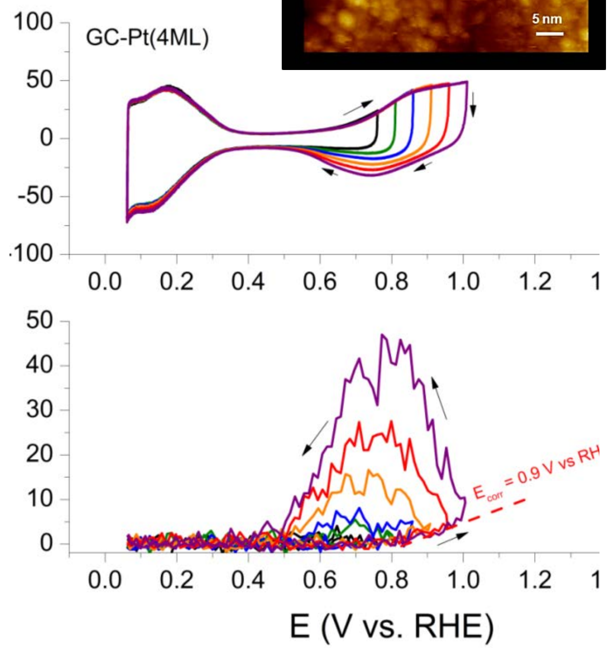


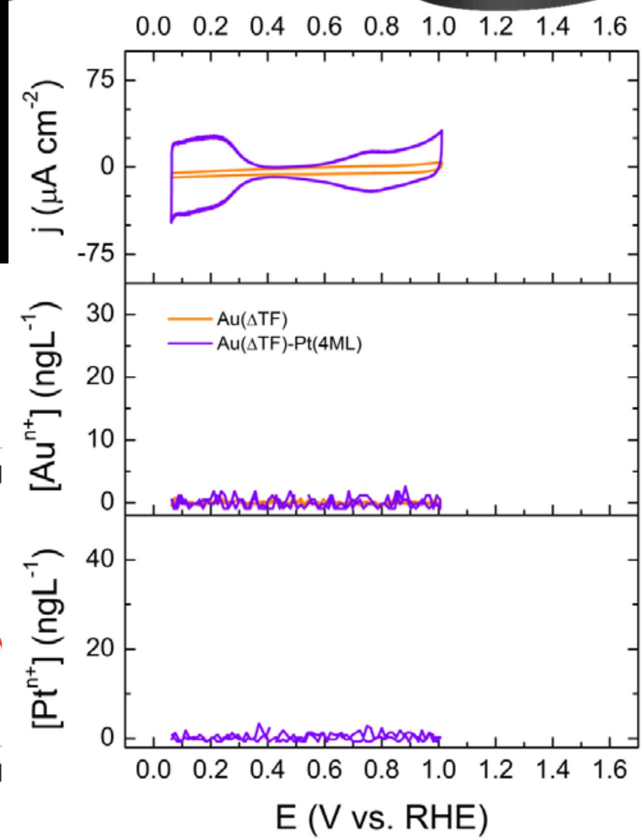



GC-Au-Pt(4ML)

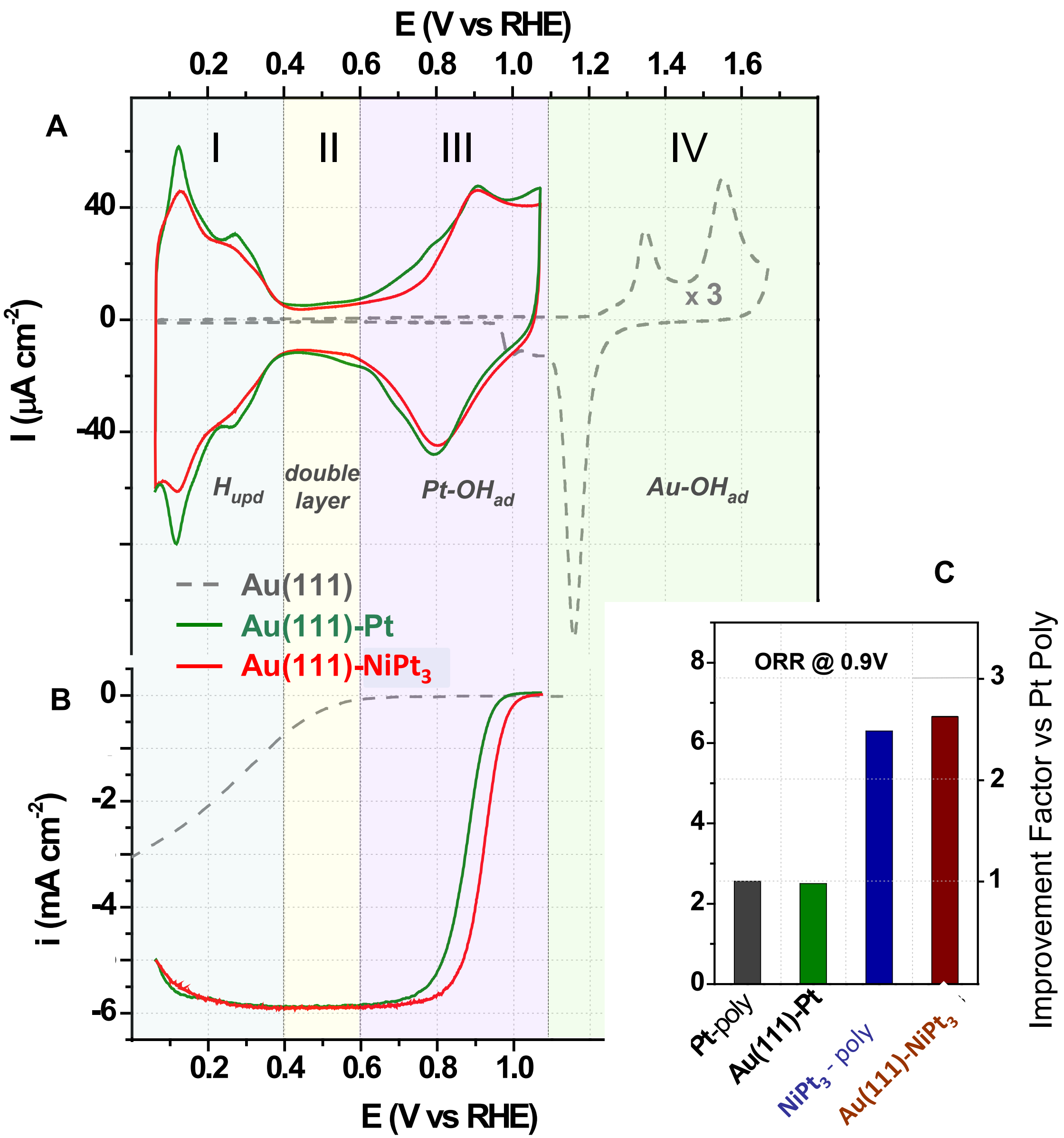
**Pt/C | 103***



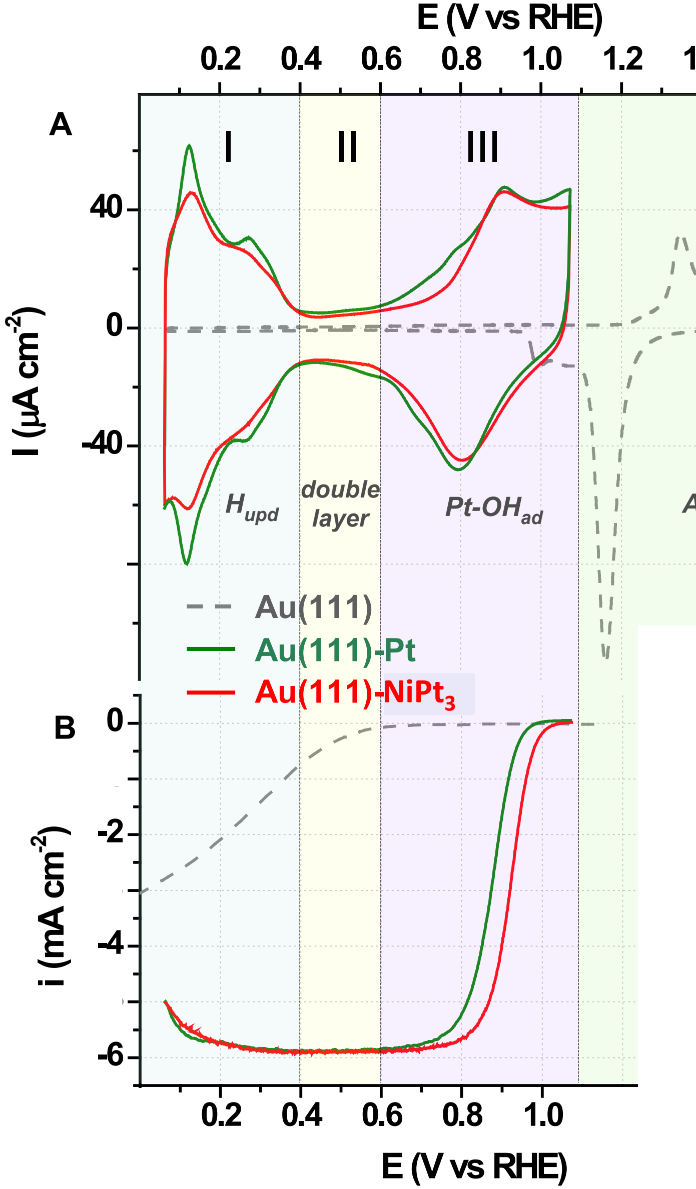



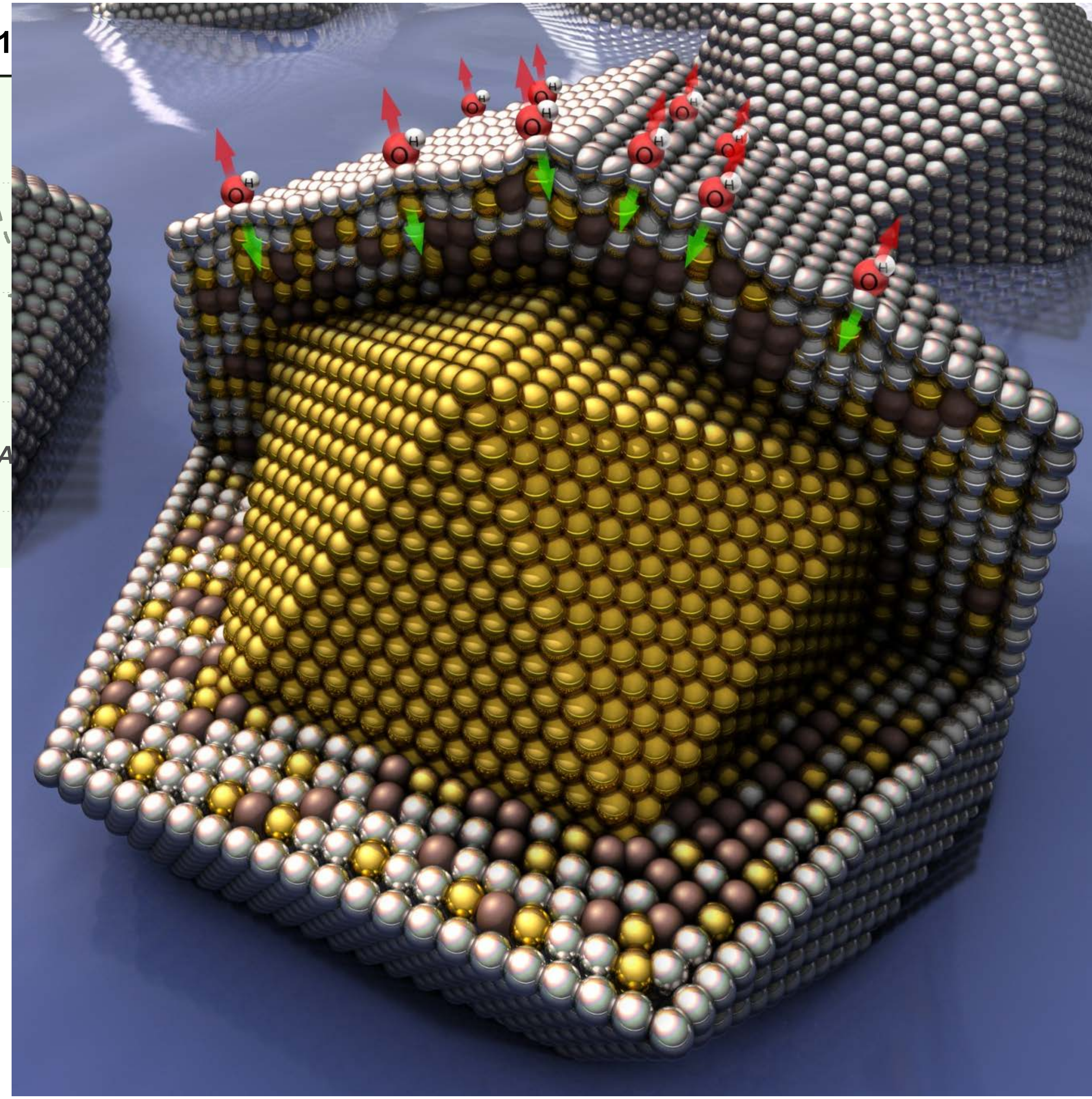



# DURABLE NPs: *Core-Interlayer-Shell Particles*

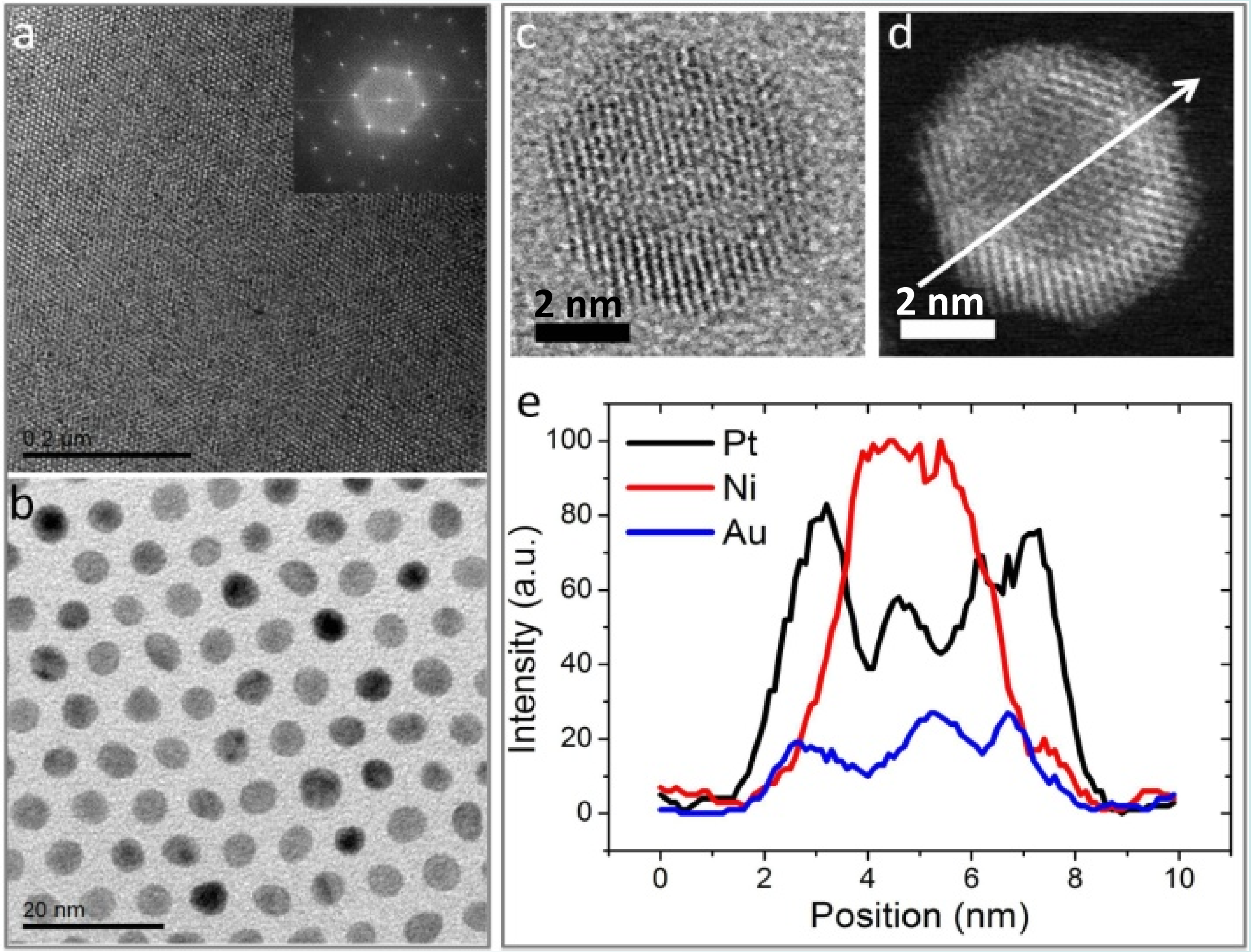


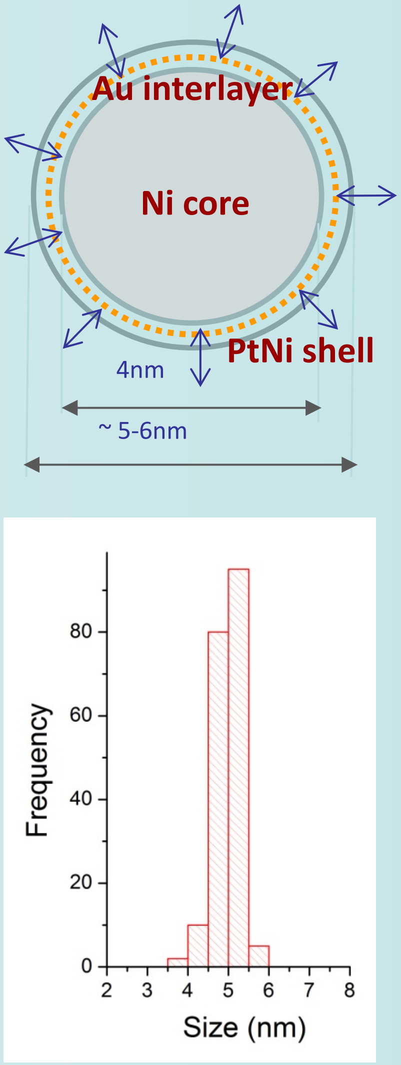
# DURABLE NPs: *Core-Interlayer-Shell Particles*



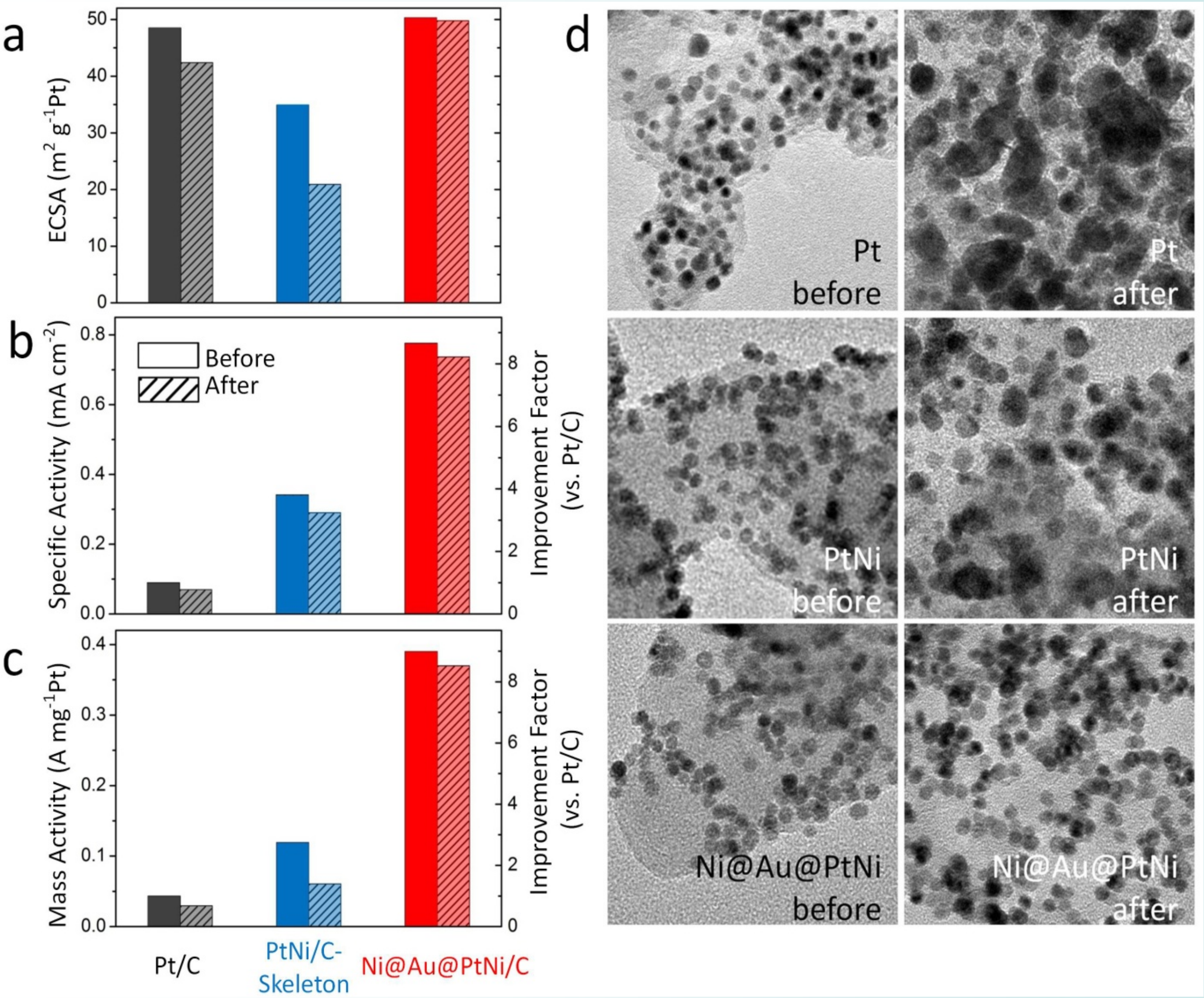
# Compositional Profile: *Core/Interlayer/Shell Electrocatalysts*



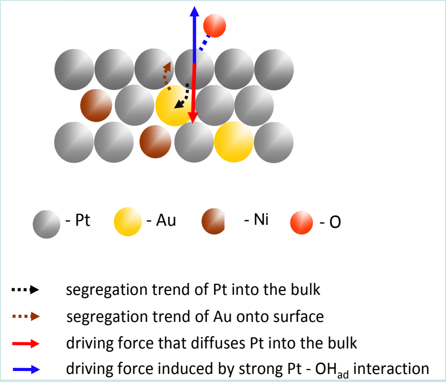



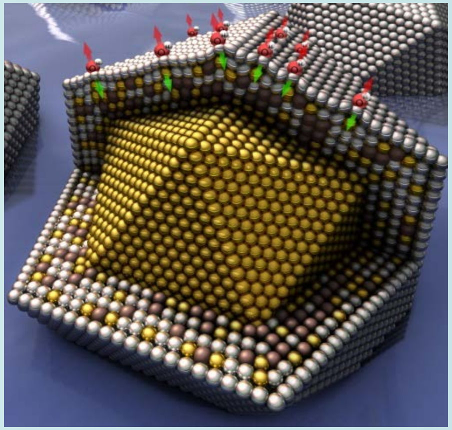

**Monodisperse , Core/Interlayer/Shell NPs: Ni core / Au interlayer / PtNi shell**

# Durable ORR Catalysts: *Core/Shell NPs with Au Interlayer*




## Stabilization mechanism

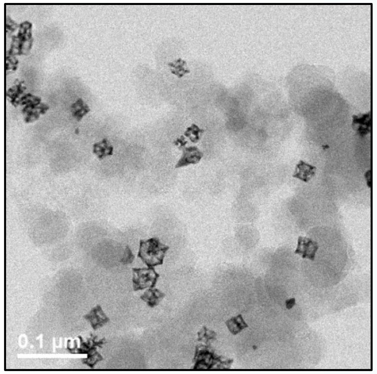


# Durable Systems: *PtNi Nanoframes in MEA*

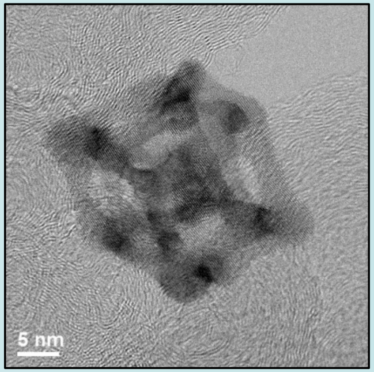
*in collaboration with Debbie Myers, ANL - CSE*

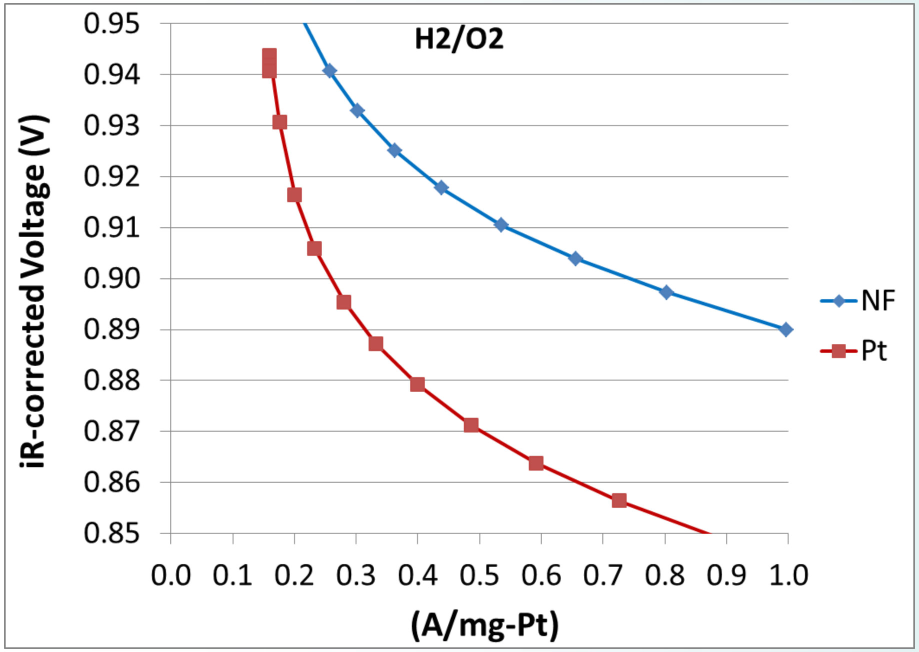
***Nanoframes in 5cm² MEA ANL and ORNL***

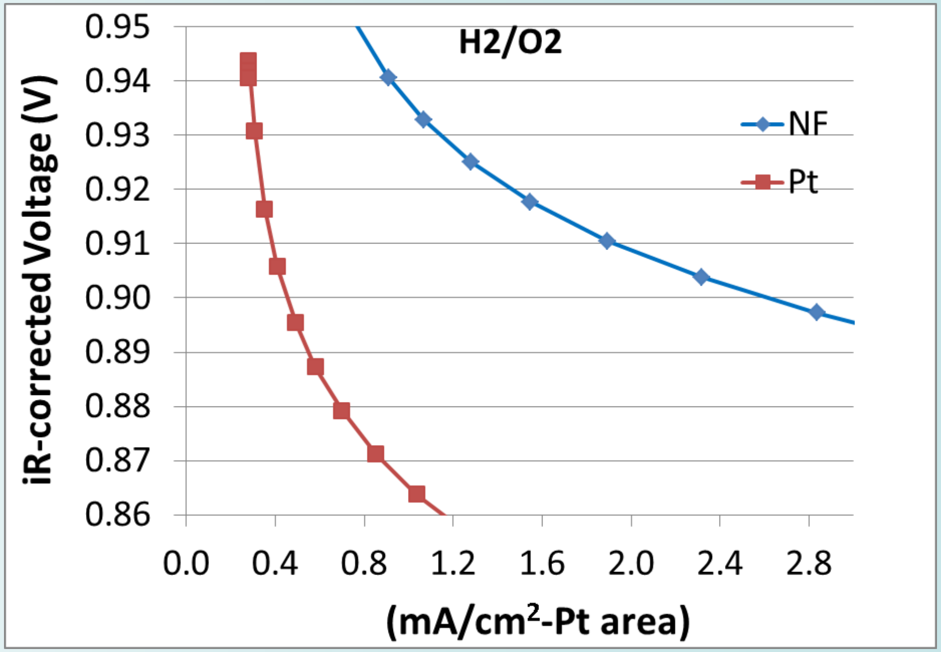



Cathode Loading: 0.035 mg-Pt/cm², I/C = 0.8
$H_2/O_2$, 80°C, 150 kPa(abs), 100%RH

| **ORR Activity @ 0.9V:** | **Mass Activity** x3.5 | **Specific Activity** x6.5 |
|---|---|---|
| TKK 20 wt%Pt/C: | 0.22 A/mg-Pt | 0.39 mA/cm²-Pt |
| **PtNi Nanoframes:** | **0.76 A/mg-Pt** | **2.60 mA/cm²-Pt** |

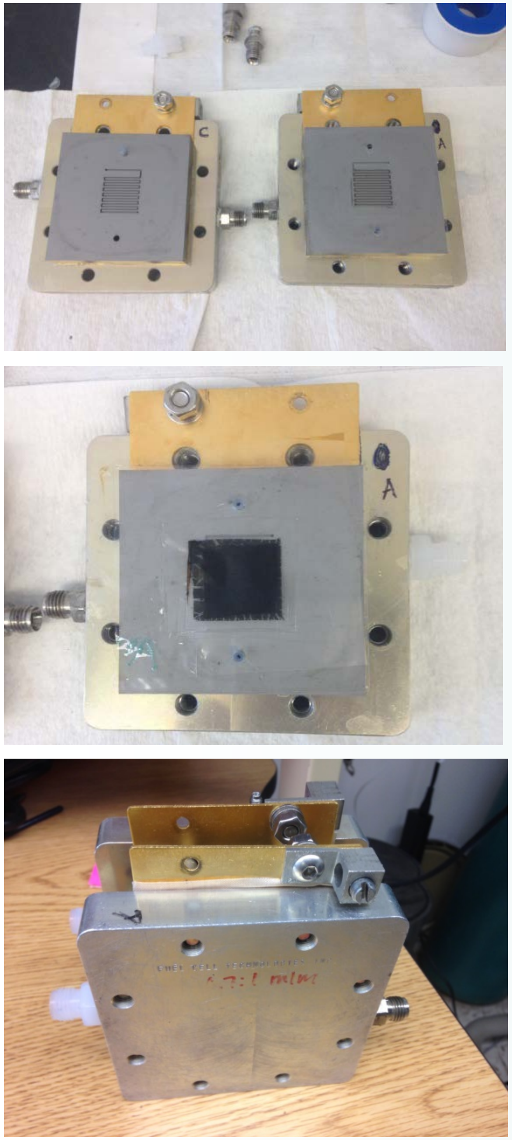


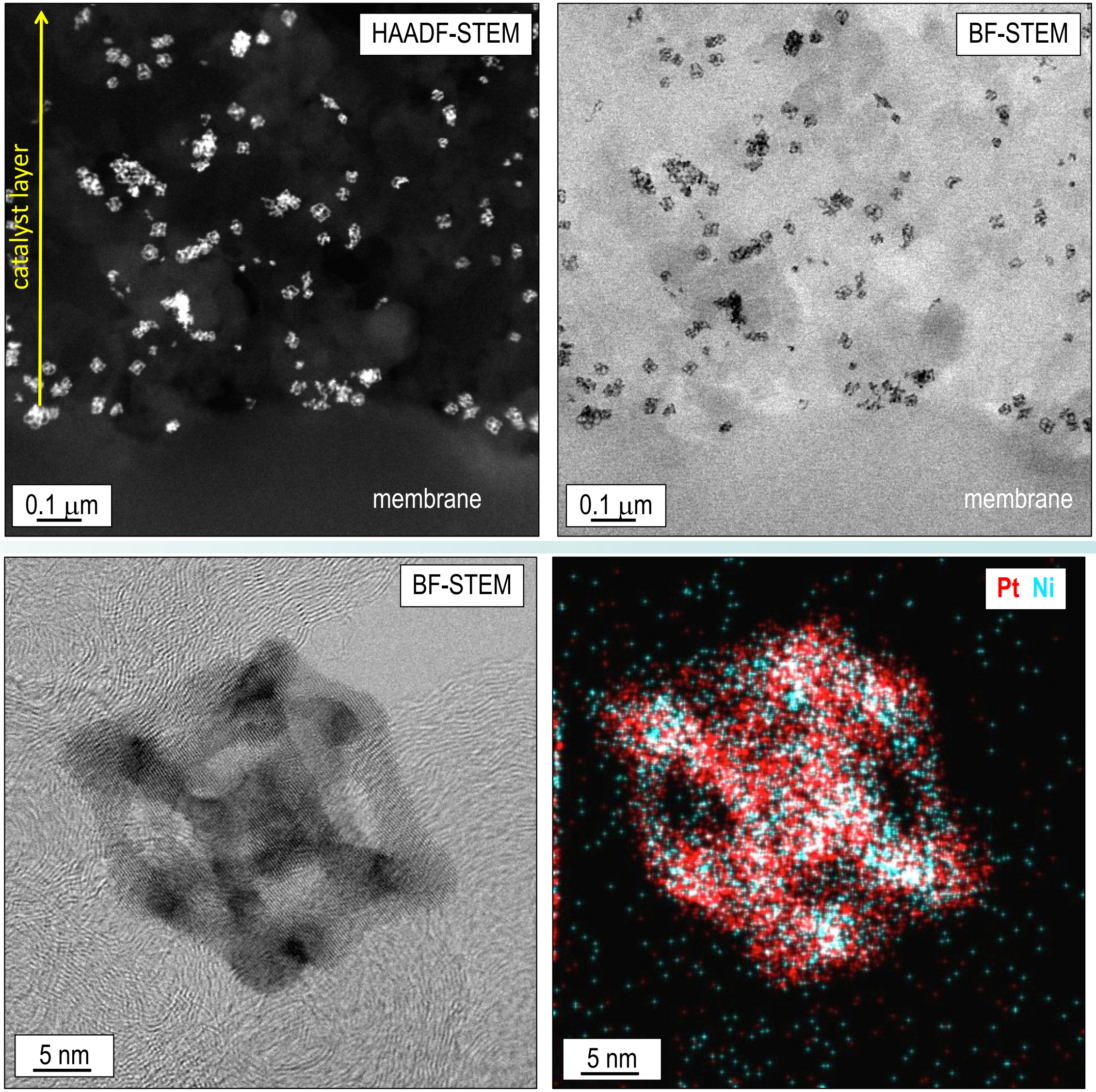



# Durable Systems: *PtNi Nanoframes (before and after)*

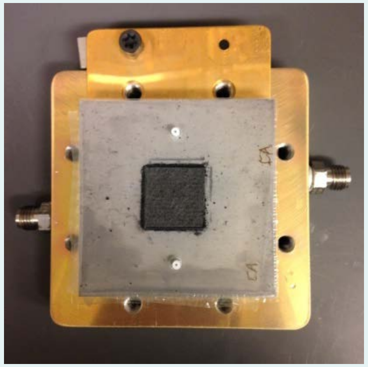
## *Nanoframes in 5cm² MEA ANL and ORNL*

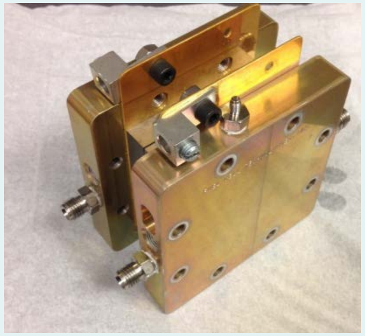


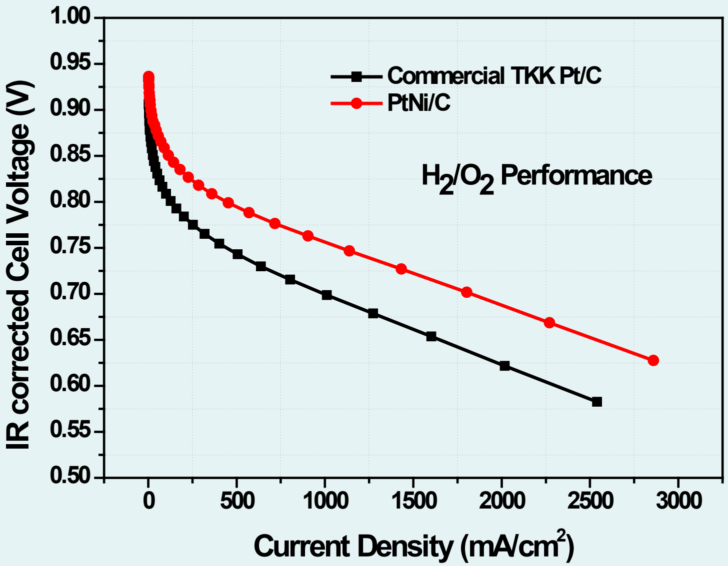


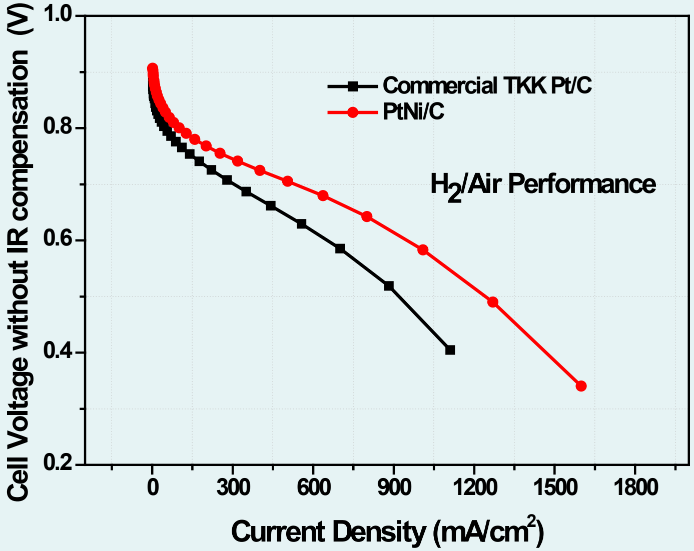
# Durable Systems: *PtNi with Multilayered Pt-Skin Surfaces*

***in collaboration with Debbie Myers, ANL - CSE***







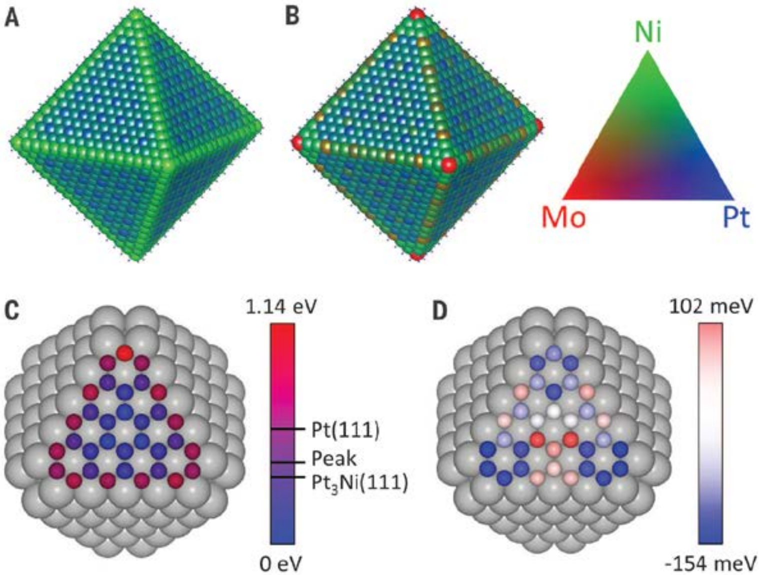

**Cathode Loading: 0.046 mg-Pt/cm²**
**I/C = 1, $H_2/O_2$ (or Air),**
**80°C, 150 kPa(abs), 100%RH**

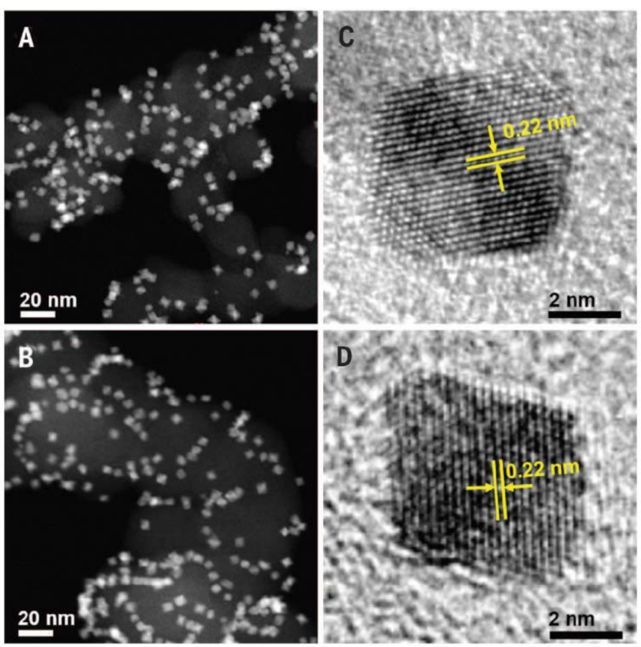
**TKK 20 wt%Pt/C**

**PtNi 16.7 wt%Pt/C**

| | Units | PtNi | TKK Pt |
|---|---|---|---|
| **Pt loading** | $mg_{PGM}/cm^2_{geo}$ | **0.045** | **0.045** |
| **Mass Activity** (H2-O2) | $A/mg_{PGM}$ @ 0.9 $V_{iR\text{-}free}$ | **0.60** | **0.27** |
| **Specific Activity** (H2-O2) | $mA/cm^2_{PGM}$ @ 0.9 $V_{iR\text{-}free}$ | **1.85** | **0.39** |
| **MEA performance** (H2-Air) | $mA/cm^2$ @ 0.8 V | **101** | **47** |
| **ECSA** | $m^2/g_{PGM}$ | **35.10** | **52.5** |

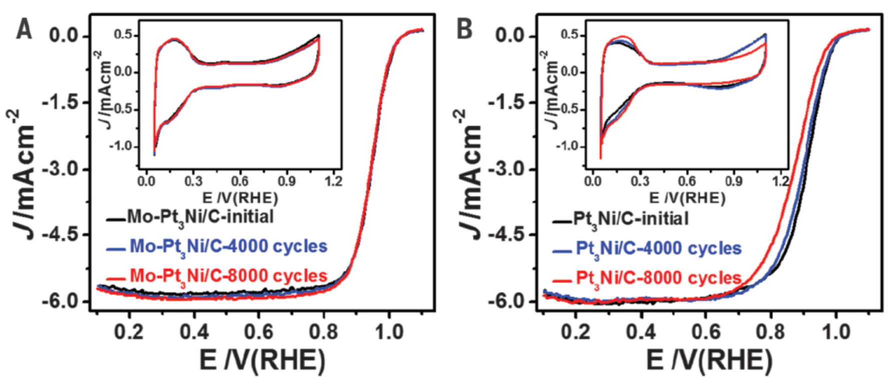
# TM doped $Pt_3Ni$ Octahedra

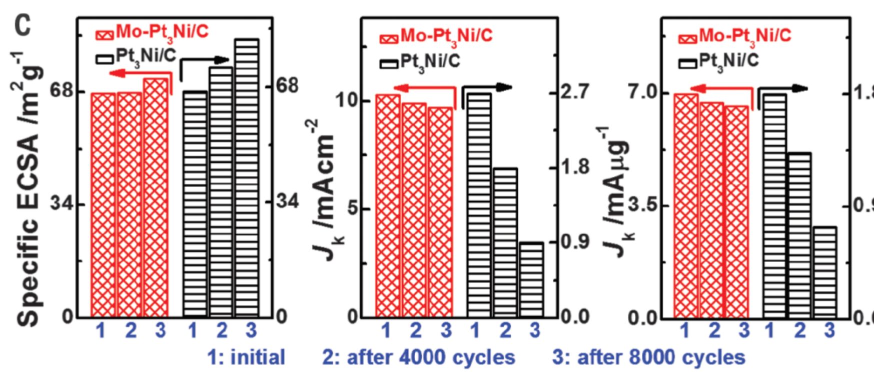



**SA and MA over 70-fold vs. Pt/C**

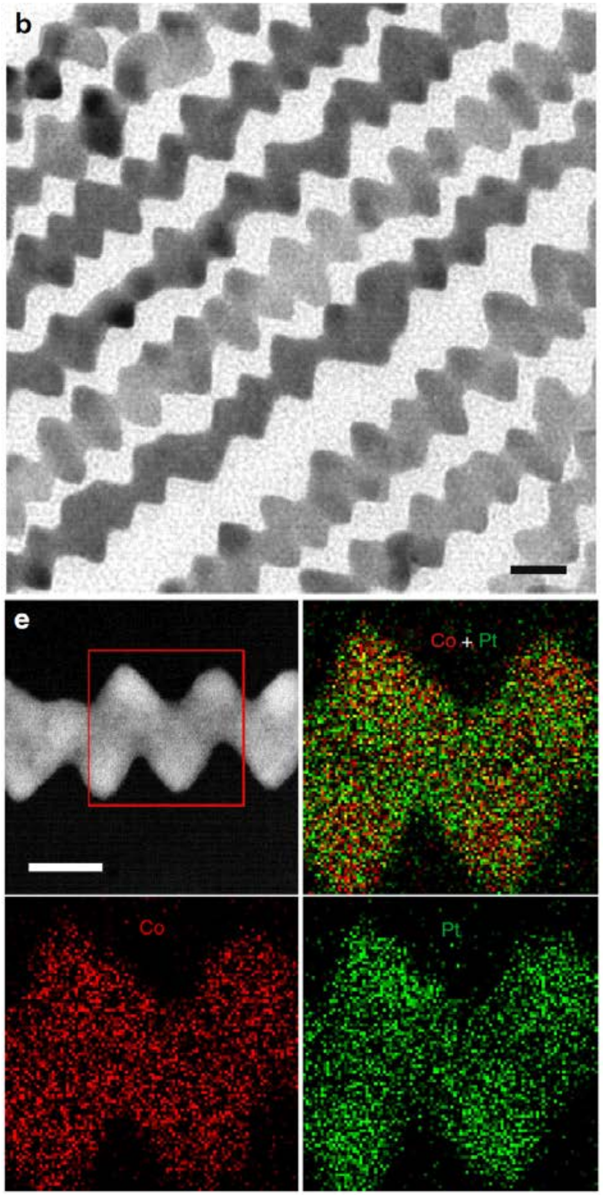
| | Catalyst | Based on $H_{upd}$: ECSA ($m^2/g_{Pt}$) | Specific activity ($mA/cm^2$) @ 0.9 V | Specific activity ($mA/cm^2$) @ 0.95 V | Mass activity ($A/mg_{Pt}$) @ 0.9 V | Mass activity ($A/mg_{Pt}$) @ 0.95 V | Based on CO stripping: ECSA ($m^2/g_{Pt}$) | Specific activity ($mA/cm^2$) @ 0.9 V | Specific activity ($mA/cm^2$) @ 0.95 V |
|---|---|---|---|---|---|---|---|---|---|
| This work | Mo-$Pt_3Ni$/C | 67.7 | 10.3 | 2.08 | 6.98 | 1.41 | 83.9 | 8.2 | 1.74 |
| This work | $Pt_3Ni$/C | 66.6 | 2.7 | 0.55 | 1.80 | 0.37 | 81.9 | 2.2 | 0.45 |
| *(53)* | PtNi/C | 50 | 3.14 | NA | 1.45 | NA | NA | NA | NA |
| *(24)* | PtNi/C | 48 | 3.8 | NA | 1.65 | NA | NA | NA | NA |
| *(21)* | $PtNi_{2.5}$/C | 21 | NA | NA | 3.3 | NA | 31 | NA | NA |
| *(28)* | $Pt_3Ni$/C nanoframes | NA | NA | NA | 5.7 | 0.97 | NA | NA | 1.48 |

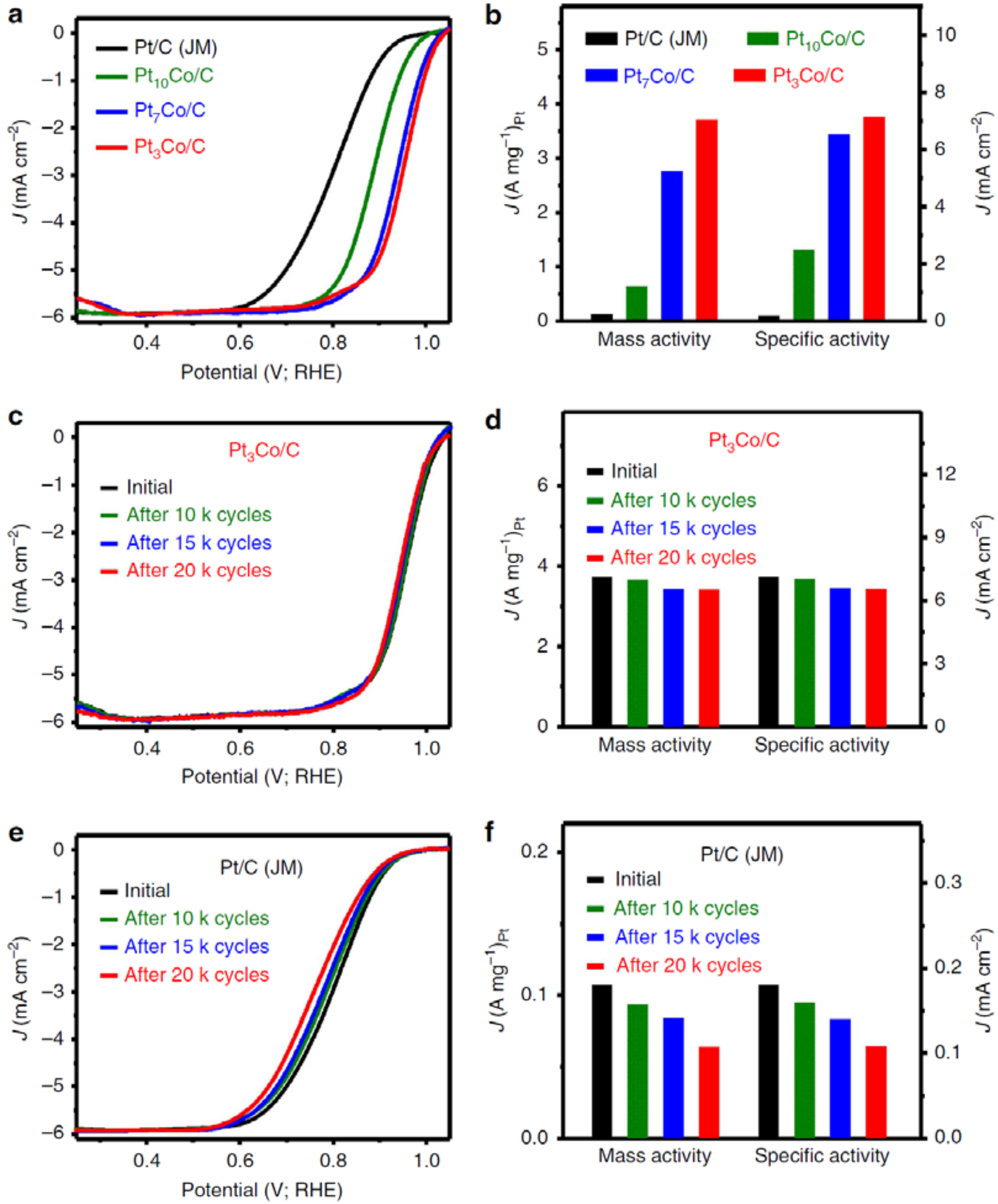



*Huang et al. Science* , 348 (2015) 1230

# Hierachical PtCo Nanowires

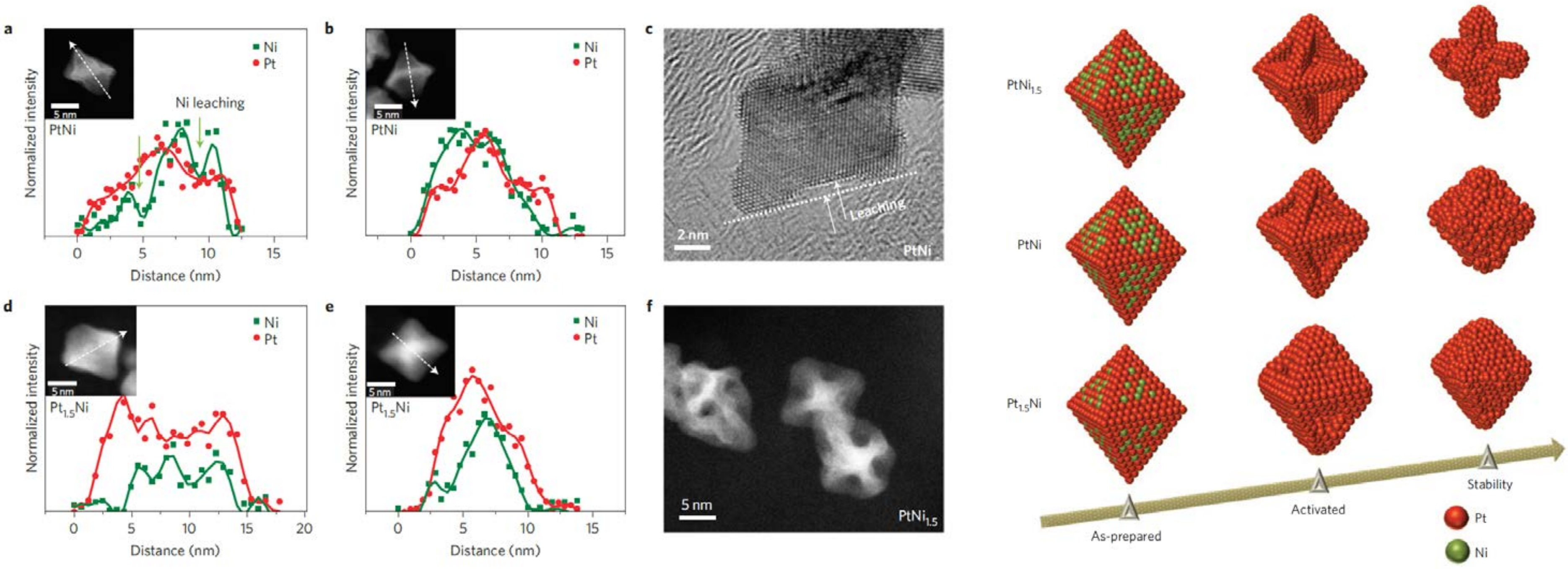


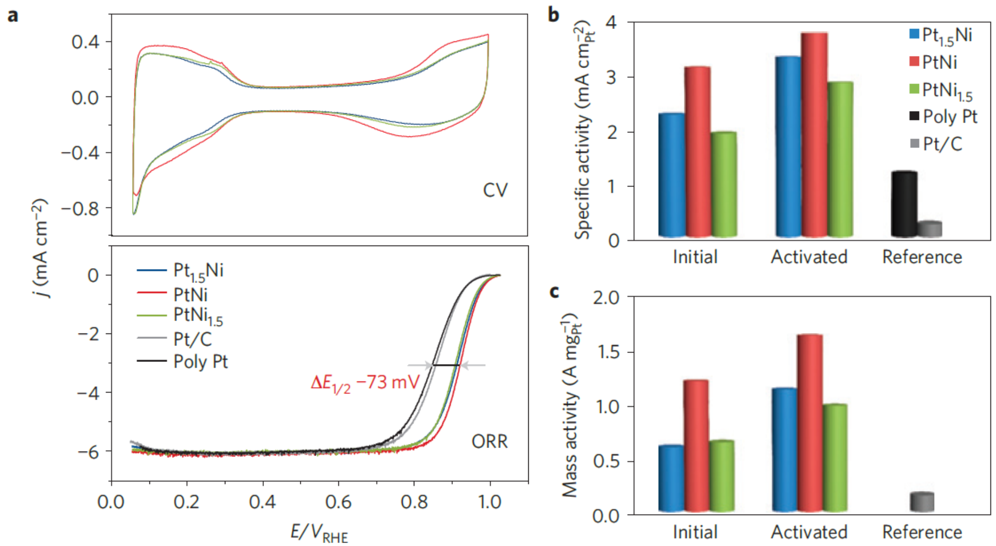




SA and MA over 30-fold vs. Pt/C

*Bu et al. Nat. Commun.* , (2016) *DOI 10.1038.natcomms11850*

# Dealloying of PtNi octahedrons

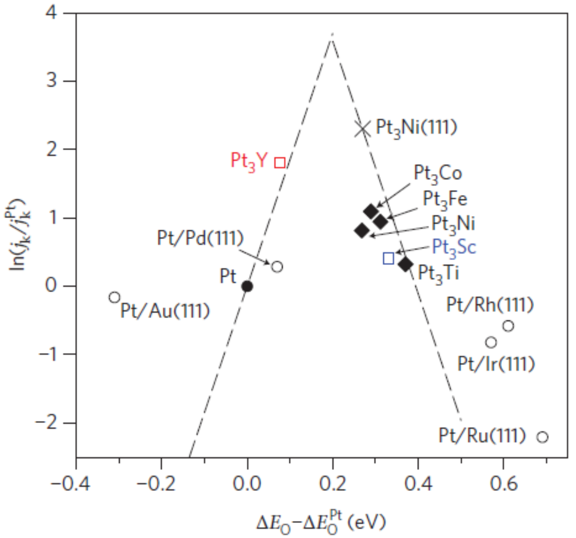


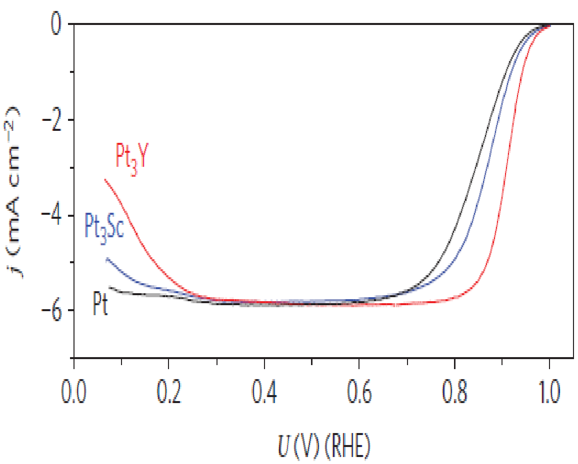



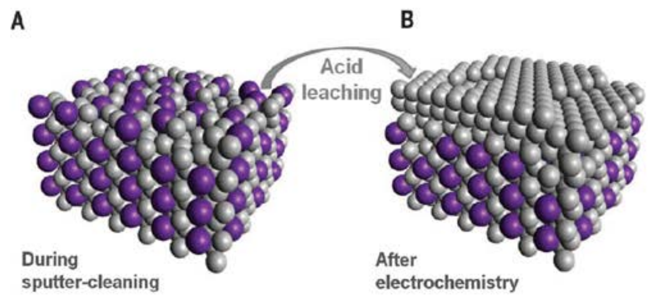

**SA and MA over 10-fold vs. Pt/C**

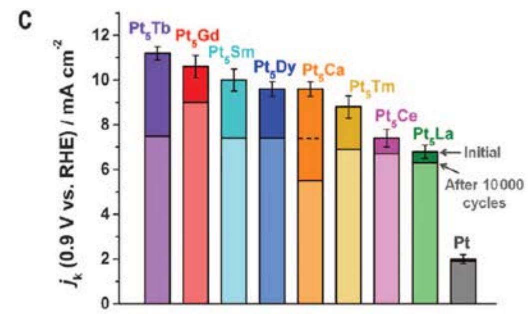
*Cui et al. Nature Mat.*, **12 (2013) 765**

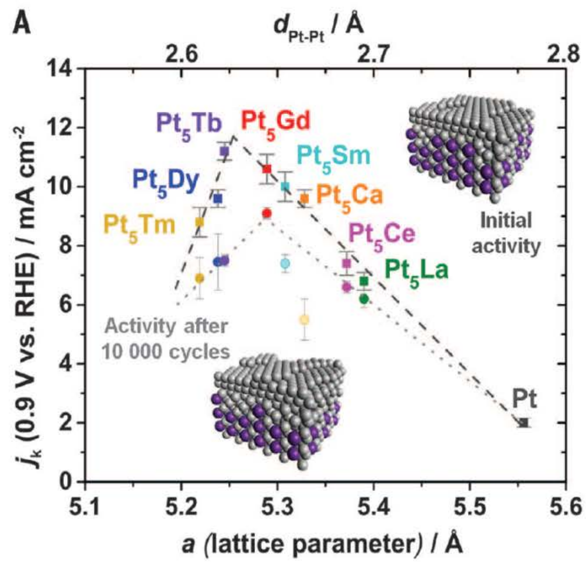
# Alloying Pt with Rare Earth Elements

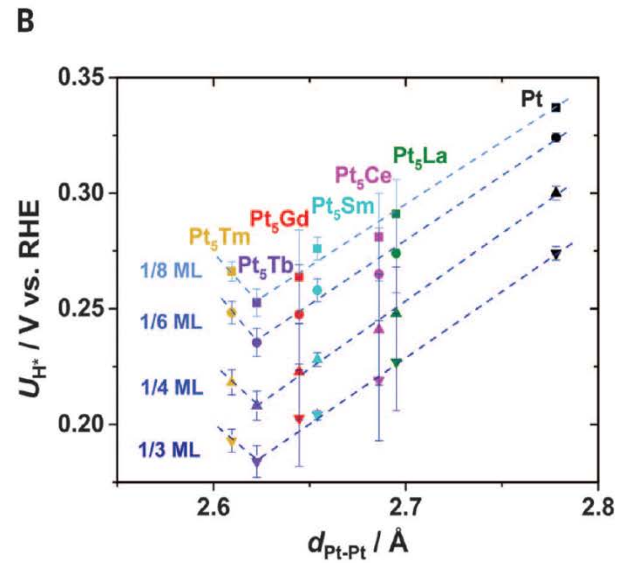


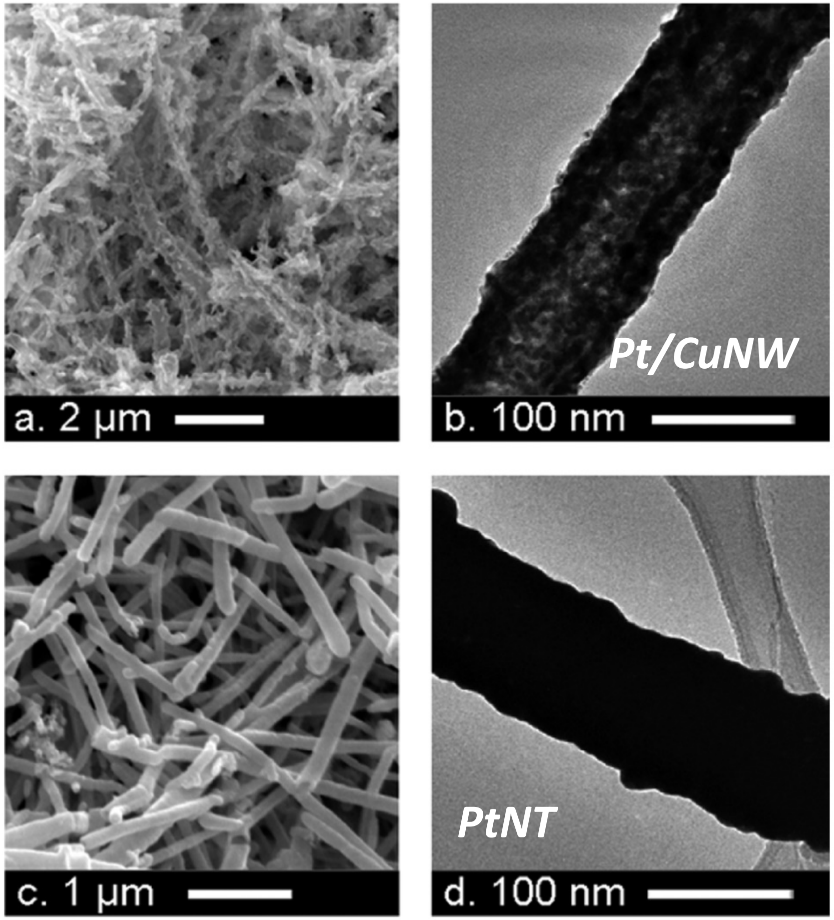



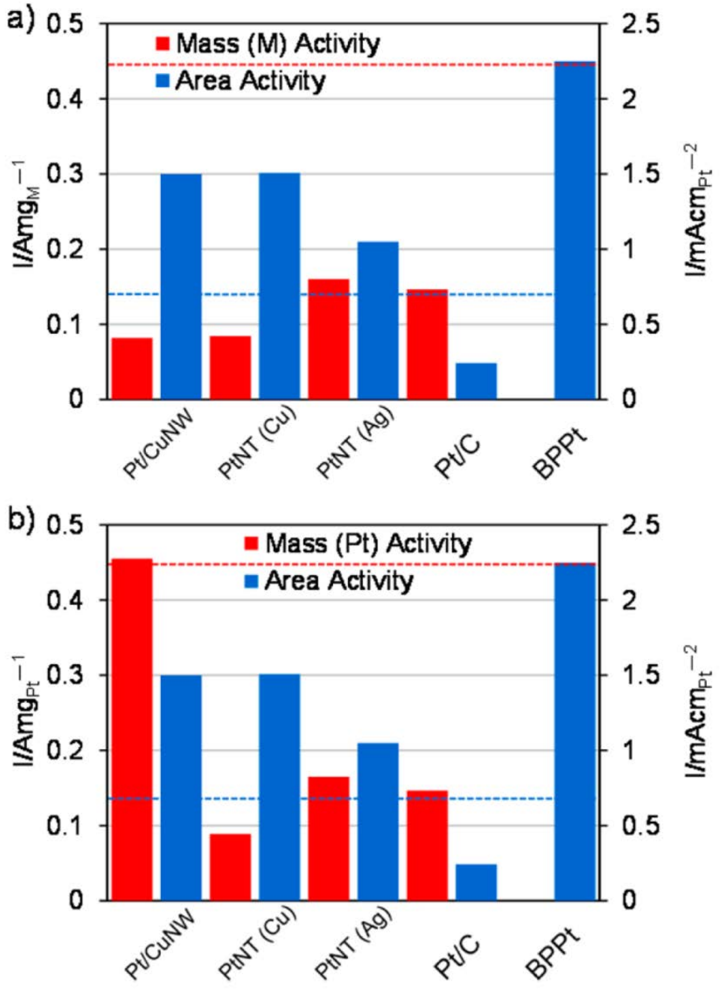

**SA over 6-fold vs. Pt/C**

*Greeley et al. Nature Chem.*, 1 (2009) 552

*Escudero-Escribano et al. Science*, 352 (2013) 73

# Pt/CuNW and PtNT




**SA and MA over 3-fold vs. Pt/C**

*Alia et al. ACS Catalysis.,* 3 (2013) 358

# Approach

## Increasing Pt monolayer activity and stability, and reducing the PGM content

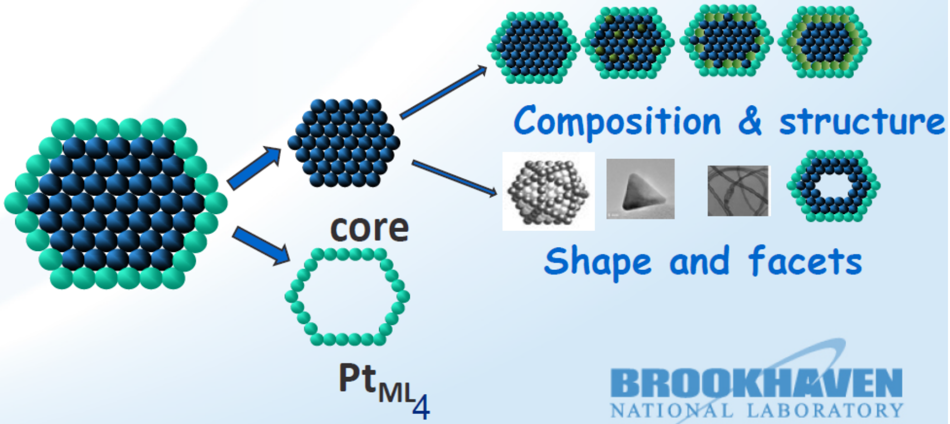
**by**

- Reducing oxygen binding energy
- Decreasing the number of low-coordination atoms
- Compressing the top layer of atoms
- Forming moderately compressed (111) facets
- Increasing stability of cores

**accomplished *via***

- Surface contraction (induced by core, hollow core, subsurface ML, segregation),
- Improving Pt ML deposition process
- Designing the cores with specific structure, composition, shape and distribution
- Electrodeposition of cores and shells to maximize catalyst utilization
- Metal-, alloy- nanowires obtained in conventional syntheses
- Refractory metal alloys used as cores

**tests, characterizations**




*J.X. Wang, H. Inada, L. Wu, Y. Zhu, Y. Choi, P. Liu, W.P. Zhou, R.R. Adzic, *J. Am. Chem. Soc, 131 (2009) 17298, JACS Select #8*

# Remaining Challenges and Barriers

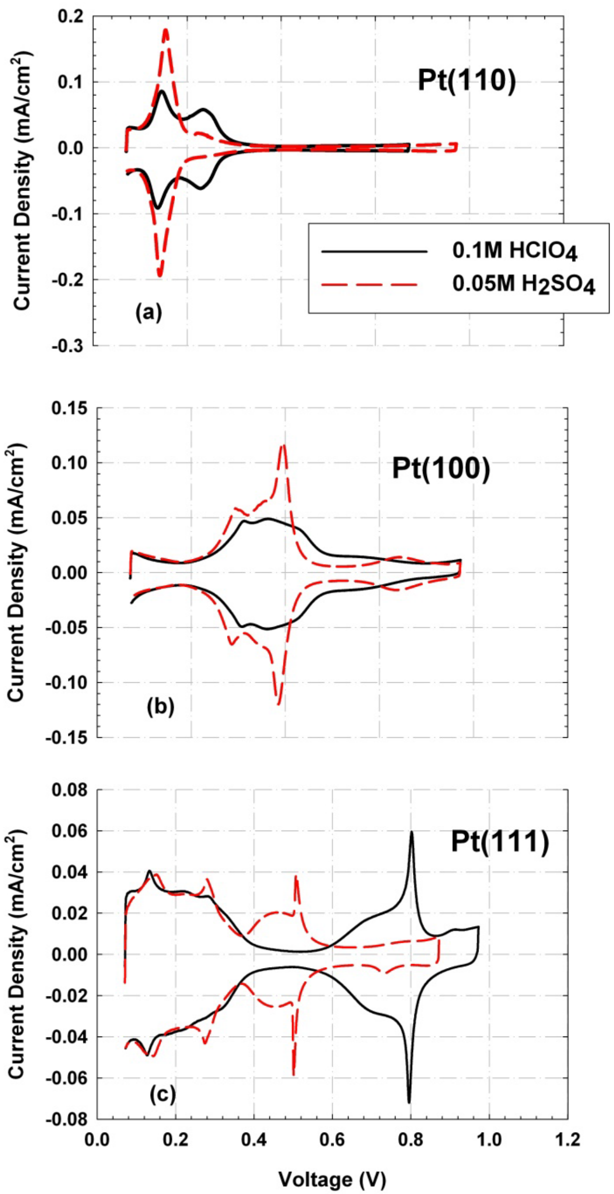
1) **Durability** of fuel cell stack (<40% activity loss)

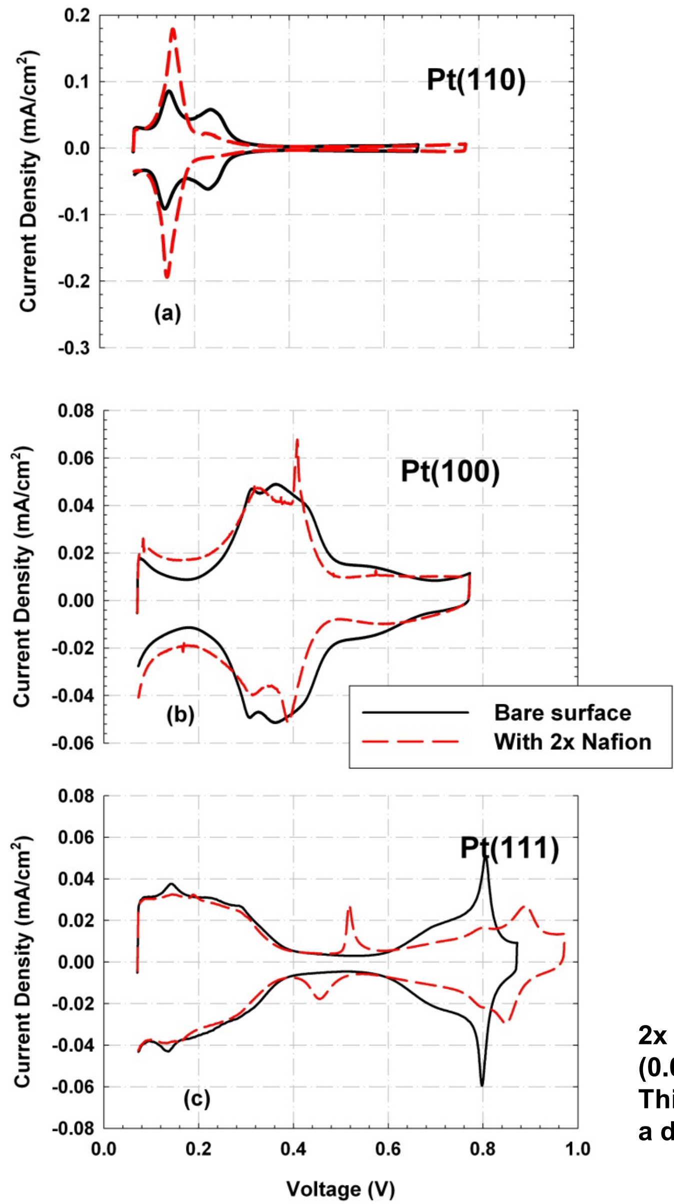
2) **Cost** (total loading of PGM 0.125 $mg_{PGM}$ / $cm^2$)

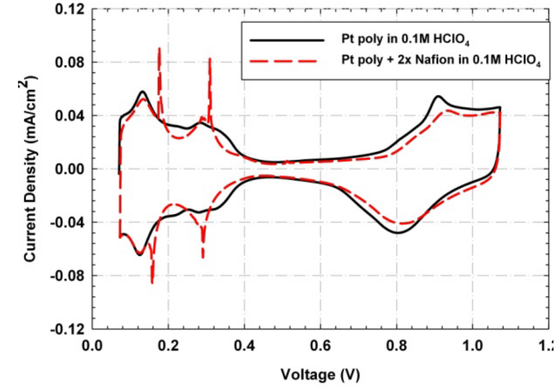
3) **Performance** (mass activity @ 0.9V 0.44 A/$mg_{Pt}$)

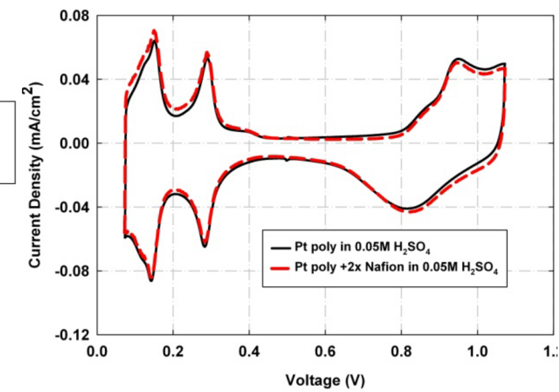
- **Differences between RDE and MEA, surface chemistry, ionomer catalyst interactions**
- **Temperature effect on performance activity/durability**
- **High current density region needs improvements for MEA**
- **Support – catalyst interactions**
- **Scale-up process for the most advanced structures**

# *Pt(hkl) with Ionomer*



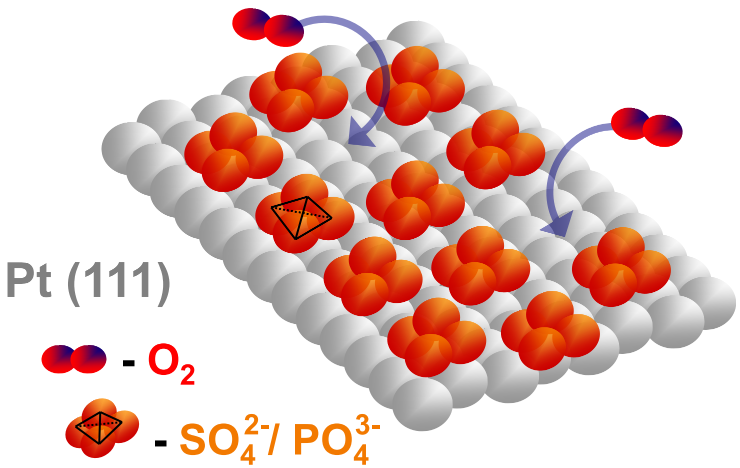



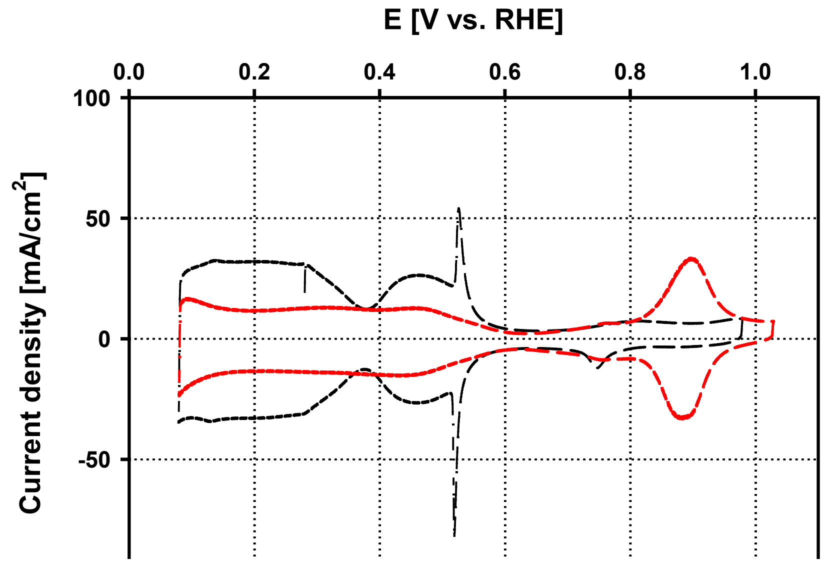



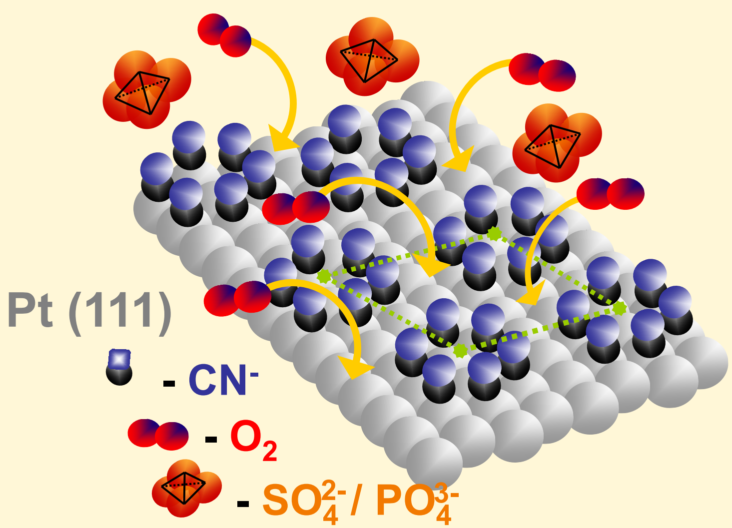

**2x refers to the case of 10 μl of solution (0.005% wt.) applied to the electrode. Thickness can then be calculated by using a dry density of 1.5 g/cm$^3$**

# Strongly Adsorbing Electrolytes: *Improving the ORR Rate*

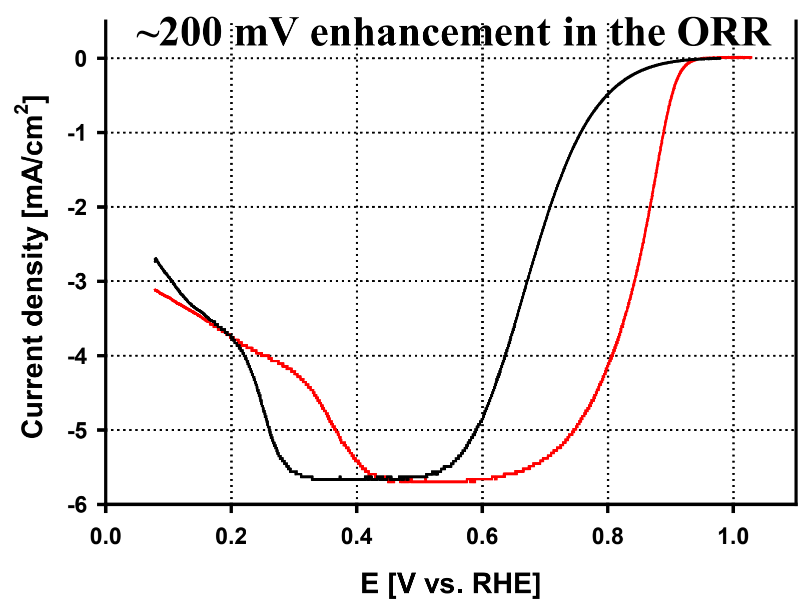



Cyanide adlayer forms (2√3x 2√3)R30º structure on Pt (111)
Itaya et al. J.Am.Chem.Soc. 118 (1996) 393

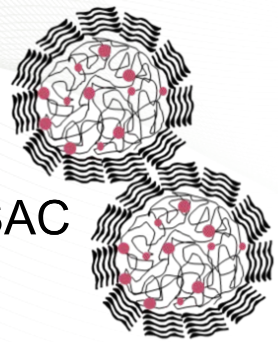



Cyanides prevent the adsorption of sulfates/phosphates

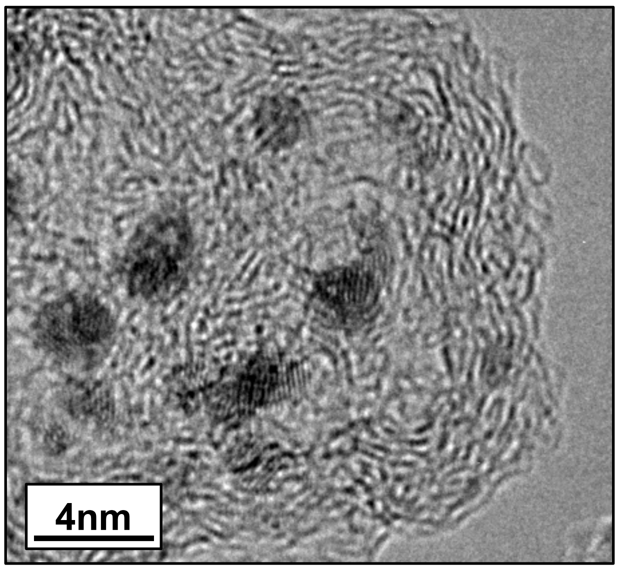


# Carbon Supports for Fuel Cell Catalysts

Pt/HSAC

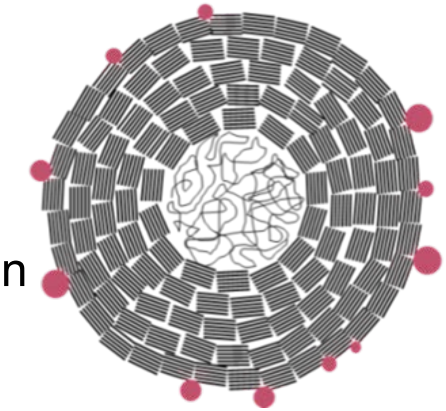


- highly disordered with meso-graphitic outer ‘shell’
- Pt “inside” carbon particles

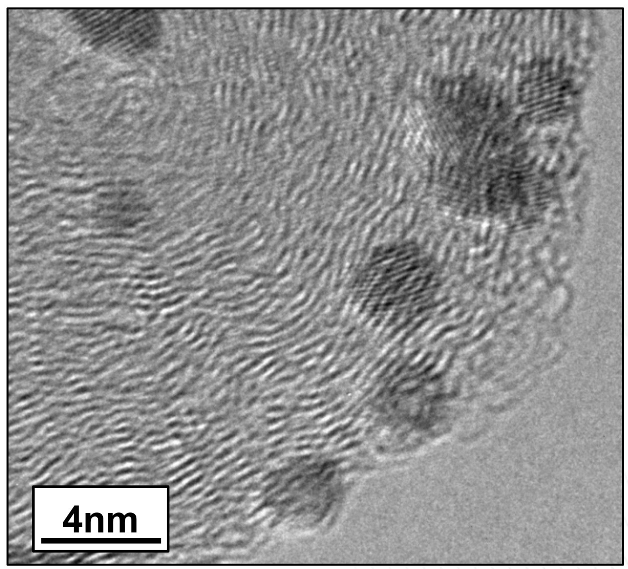



<

Pt/Vulcan

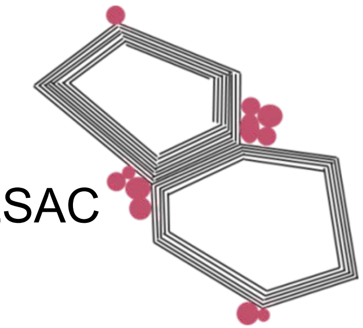


- concentric ‘domain’ structure ~4-5 nm graphite domain size
- Pt on surface of carbon particles

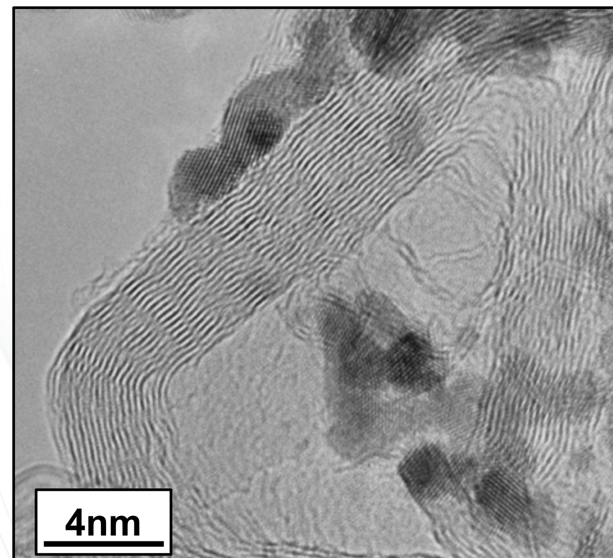



<

Pt/LSAC



- highly ordered/faceted graphitic ‘shell’ with hollow core

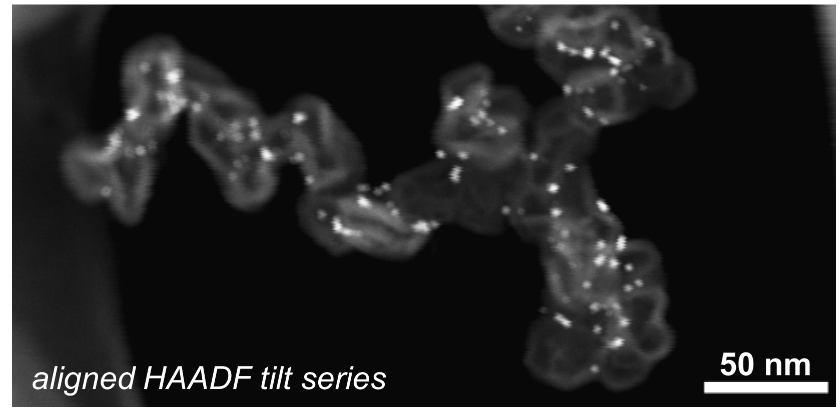


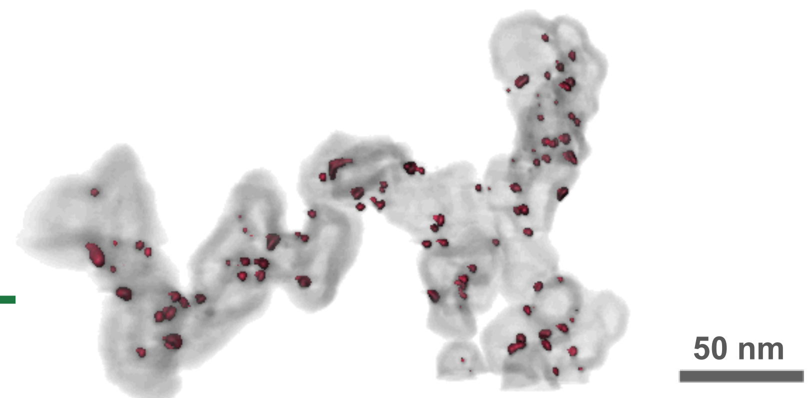



Oak Ridge National Laboratory

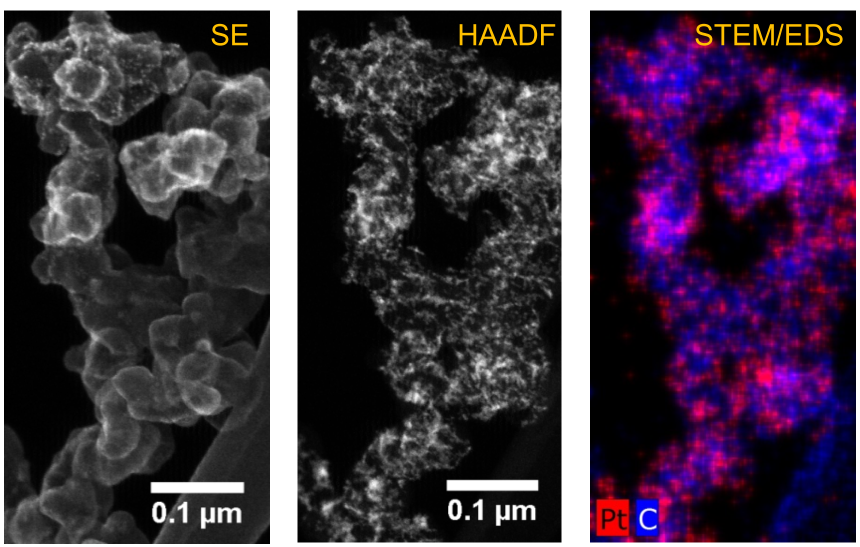
# Imaging Catalyst Distributions in 3D

- Quantify initial catalyst dispersions on different carbon supports ⟶ agglomeration
- Elucidate catalyst degradation mechanisms (Pt agglomeration, coarsening, dissolution)
  ⟶ AST for catalyst degradation
  30,000 cycles 0.6-1.0V
- Improve stability and durability of catalyst/support through structural optimization




*segmentation, visualization, and quantitative analysis*

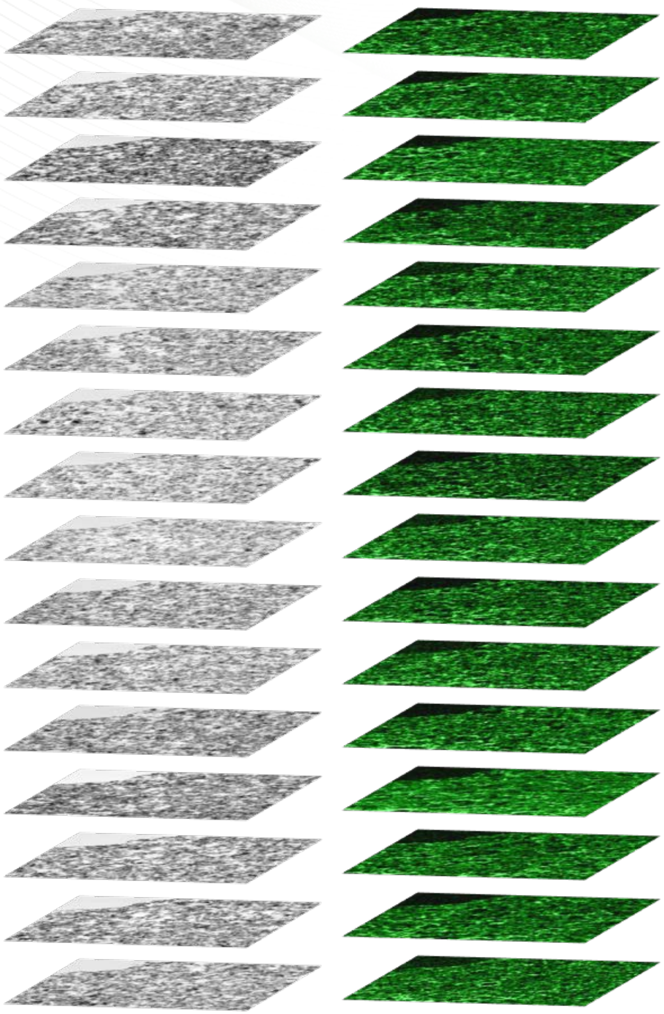





OAK RIDGE National Laboratory

# *Technical Accomplishments and Progress*: Imaging Ionomer Dispersions in Catalyst Layers in *3D*

17 MEA slices

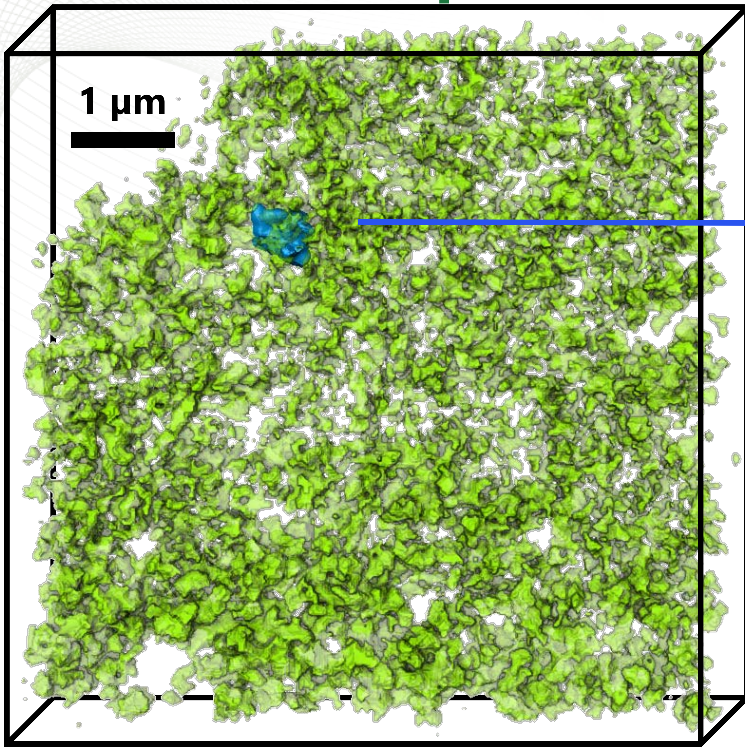



Individual F maps acquired from "slices" are stacked to create a ***3D rendering/reconstruction*** of the ionomer distribution within a given volume of the CL

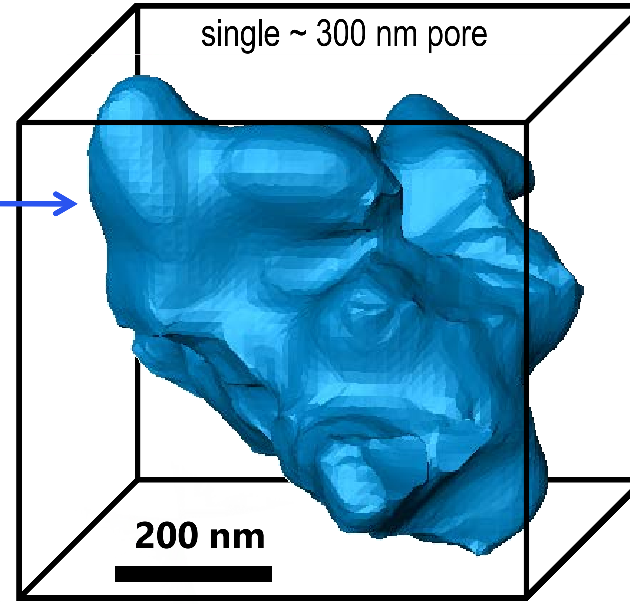


OAK RIDGE National Laboratory

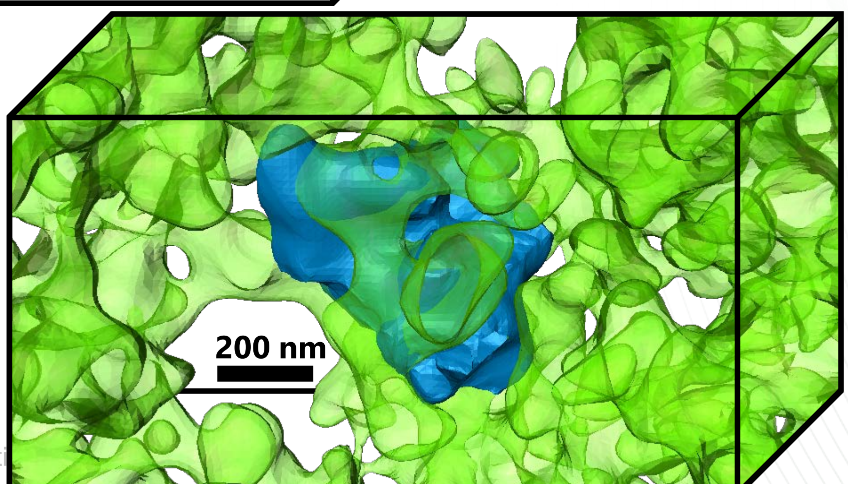
# *Technical Accomplishments and Progress*: Imaging Ionomer Dispersions in Catalyst Layers in *3D*

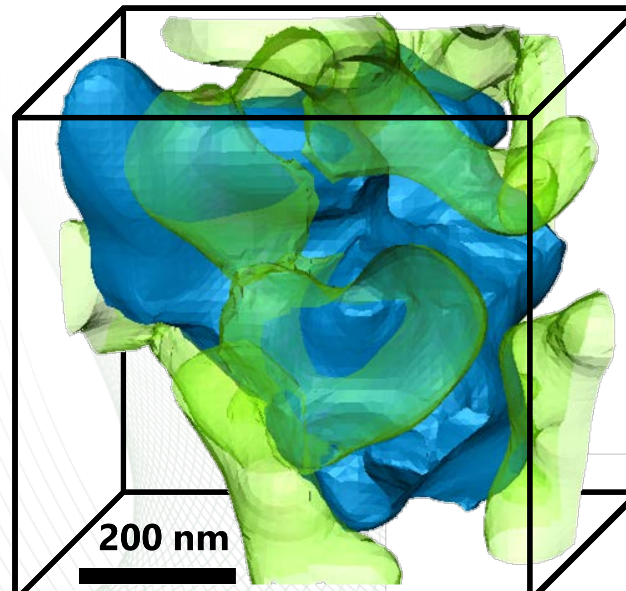



To correlate ionomer with porosity (and simplify visualization), a single secondary pore is selected from CL volume using corresponding STEM images




**Same pore with ionomer**



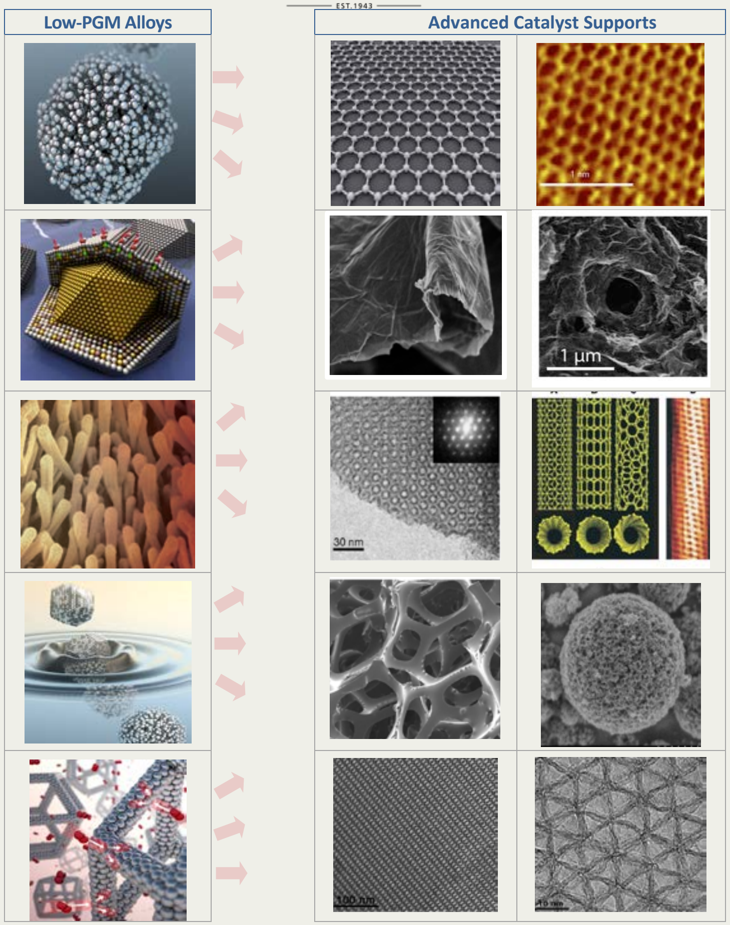
# Collaborations

Argonne National Laboratory — **Lead:** design, synthesis, evaluation

Berkeley Lab — **Sub:** synthesis, scale-up support

Oak Ridge National Laboratory — **Sub:** structural characterization

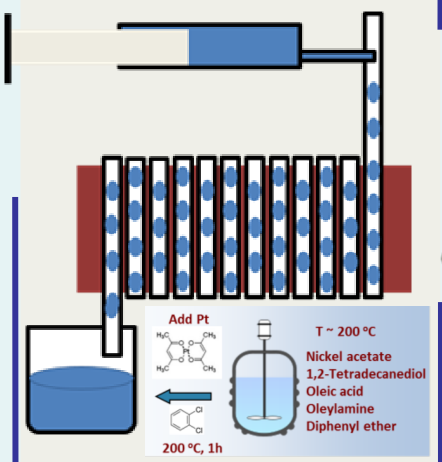
Los Alamos National Laboratory — **Sub:** catalyst supports




***Low-PGM Alloy Catalysts***

Argonne National Laboratory — **Lead:** process R&D and scale-up

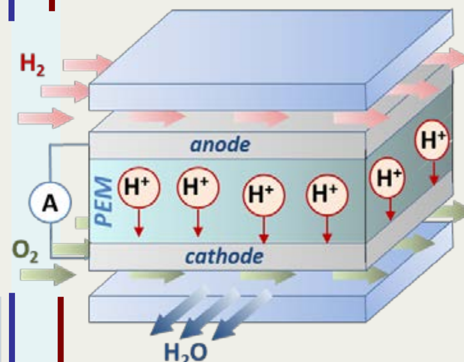
Berkeley Lab — **Sub:** process support




***Catalysts Scale Up***

Argonne National Laboratory — **Lead:** 5 and 25cm² MEA

Los Alamos National Laboratory — **Sub:** 25 and 50cm² MEA

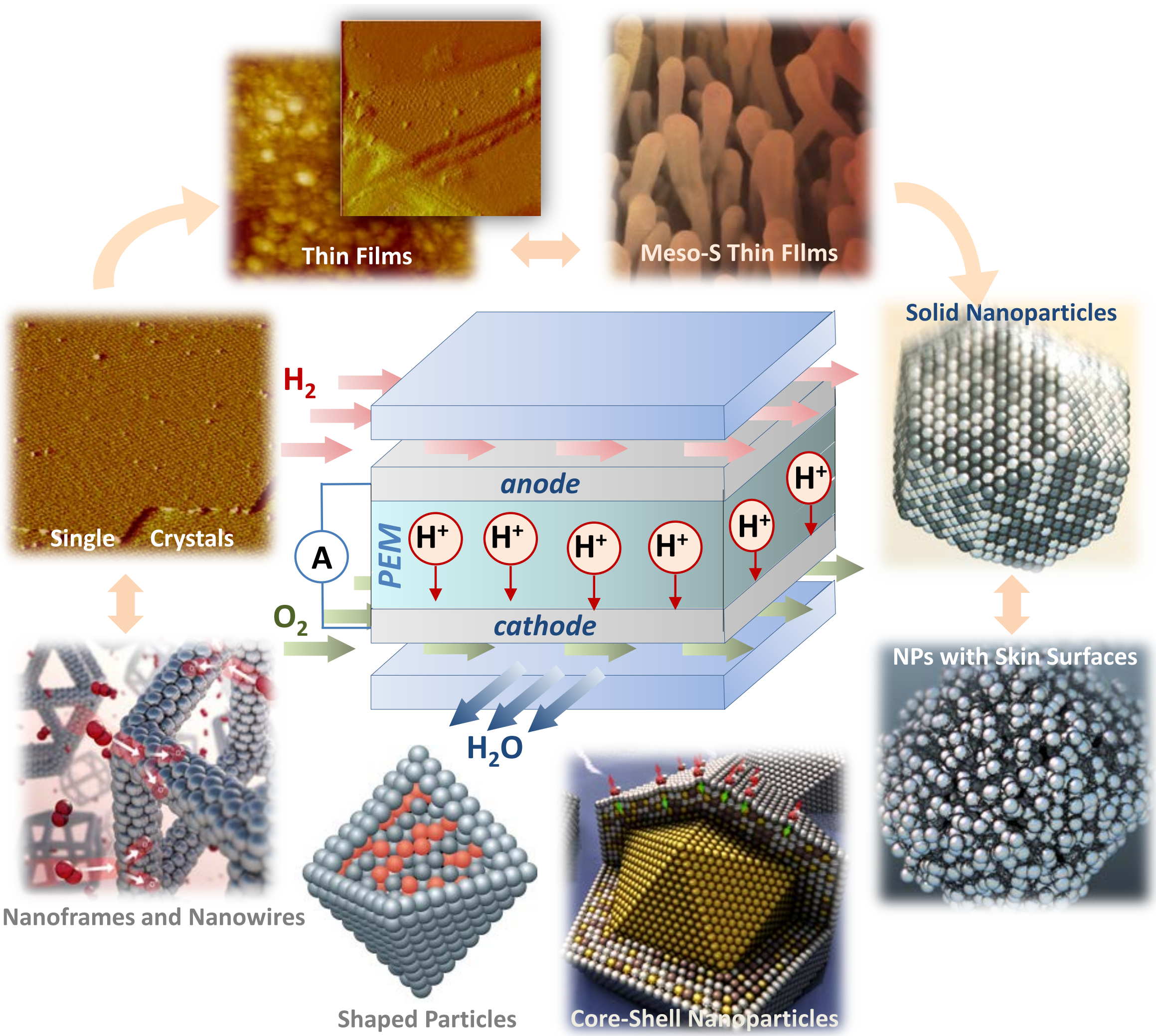



***MEA***

***OEMs***

**T2M**

# APPROACH




**RDE**

↓

**MEA**

↓

**Toyota - *Mirai***

*Principal Investigators:* Vojislav Stamenkovic
Nenad Markovic

*Full time postdocs:* Dongguo Li (RDE, synthesis, thin films)
Haifeng Lv (RDE, synthesis, MEA)
Rongyue Wang (scale up syntehsis, RDE, MEA)

*Partial time postdocs:* Pietro Papa Lopes (RDE-ICP-MS)

*Partial time Staff:* Paul Paulikas (UHV, thin films)
Dusan Strmcnik

*Grad student:* Nigel Becknell (synthesis, RDE, EXAFS)

*Collaborators:* Guofeng Wang, University of Pittsburgh
Jeff Greeley, Purdue University
Plamen Atanassov, University of New Mexico
Debbie Myers, Argonne National Laboratory
Rod Borup, Los Alamos National Laboratory
Karren More, Oak Ridge National Laboratory
Peidong Yang, University of California Berkeley

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Yijin Kang, ANL (UESR)

Nemanja Danilovic, ANL (ProtonOnSite)

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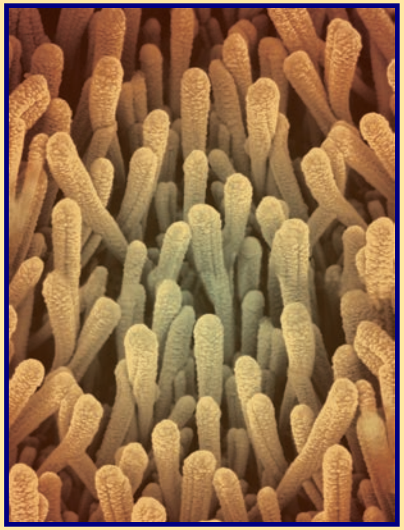

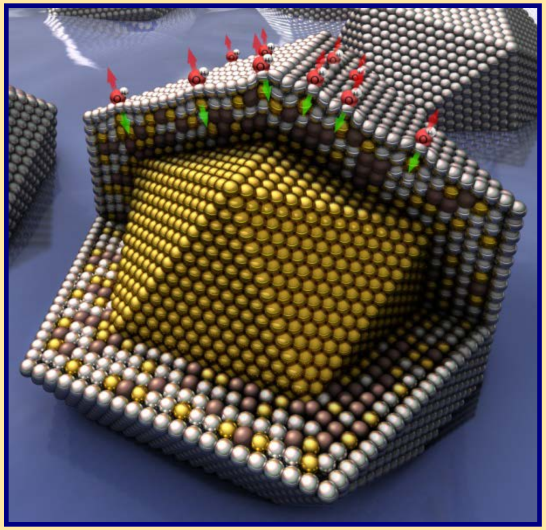

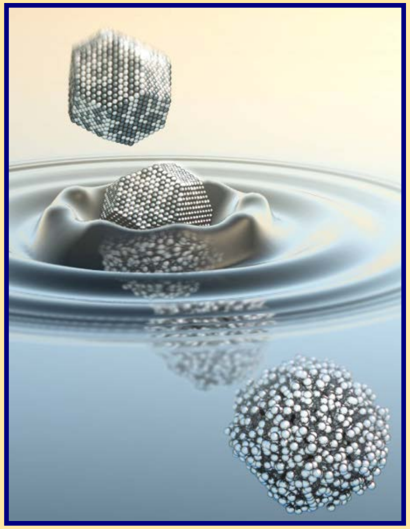

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# Thank you

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DOE Fuel Cell Technologies Office

**Voya (Vojislav) Stamenkovic**
Argonne National Laboratory

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