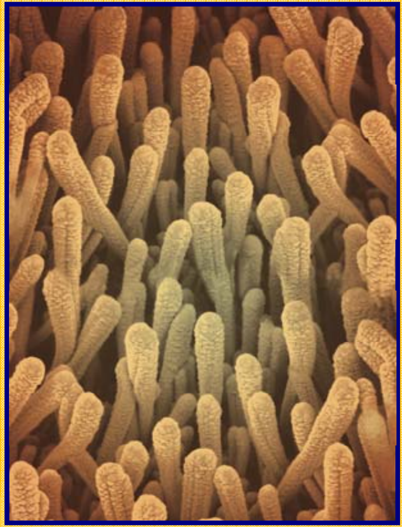
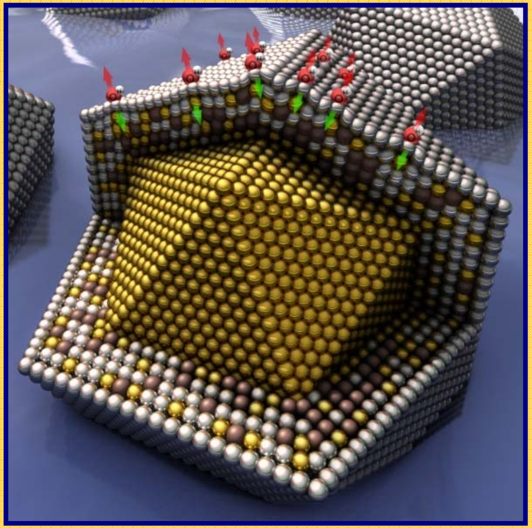
Electrocatalysts with Ultra Low PGM Loadings

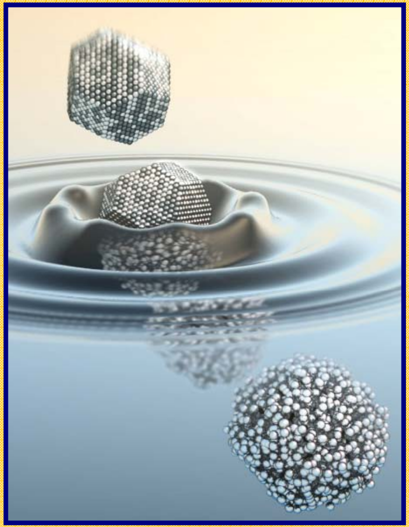
Materials Science Division

Argonne National Laboratory

Vojislav Stamenkovic and Nenad Markovic







CWG Meeting, Los Alamos, New Mexico

January 21, 2015

Argonne NATIONAL LABORATORY

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HYUNDAI NEW THINKING. NEW POSSIBILITIES.

VEHICLES SHOPPING TOOLS WHY HYUNDAI FIND A DEALER

Introducing the

2015 **Tucson Fuel Cell**

$499/month 36-month lease
$2,999 due at lease signing

Introducing the Tucson Fuel Cell, Hyundai's first-ever, hydrogen-powered vehicle with zero-emissions.

An EV for people on the move.

It takes less than 10 minutes to fully fill the Tucson Fuel Cell, compared to current EVs, which require at least 3 hours with a 240V charge, or a minimum of 14 hours* with a 110V charge.

POWERTRAIN

Fuel System:	Hydrogen Fuel Cell
Horsepower (est.):	134 hp @ 5,000 rpm*
Torque (est.):	221 @ 1,000 rpm*
Fuel Cell Type:	Proton Exchange Membrane
Fuel Cell Power (max):	100 kW
Electric Motor Type:	Induction
Electric Motor Power (max):	100 kW
Fuel Tank Capacity:	12.4 lb. (5.64 kg.) at 10,000psi
Battery Type:	Li-Polymer
Battery Energy:	0.95 (kWh)
Battery Power (max):	24 kW
Battery Capacity:	60 AH

PERFORMANCE (est'd)

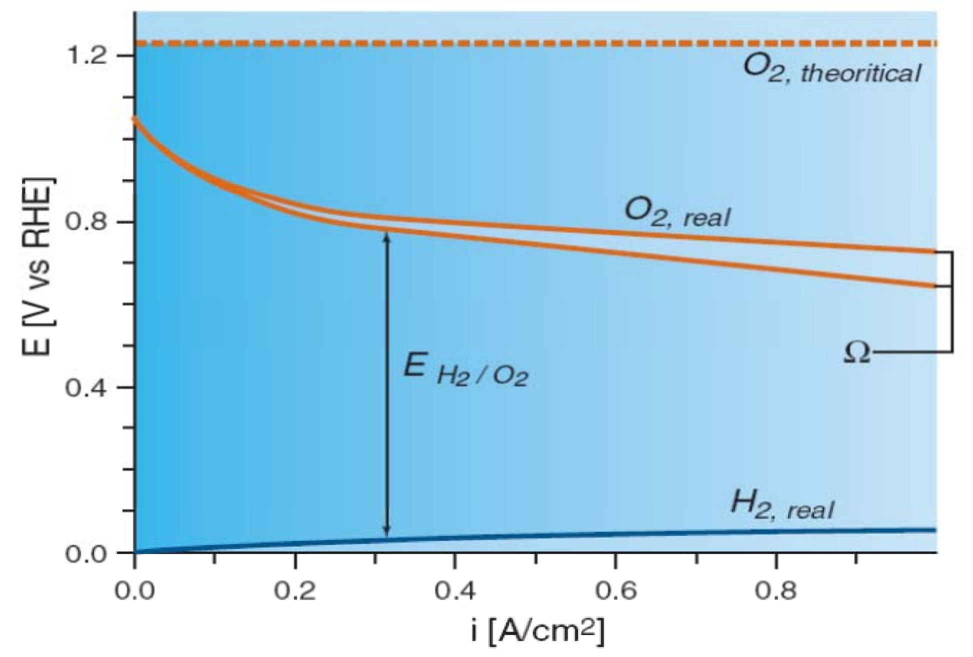
CO2 Emission (g/mile):	0
Max. Driving Range (per tank):	265 miles**
Max. Vehicle Speed (mph):	100
Acceleration (0-62 mph):	12.5 sec
Single-speed transmission FWD miles-per-gallon equivalent (city/hwy/comb.)	49 / 51 / 50
Hydrogen tank capacity (liters/gallons)	144 / 38

ORR: *cathode limitations*

DOE Technical Targets

- Specific activity @0.9$V_{iR\text{-}free}$: 720 μA/cm^2
- Mass activity @0.9V: 0.44 A/mg_{Pt}
- Electrochemical area loss: < 40%
- Catalyst support loss: < 30%
- PGM Total content: 0.2 g/kW
- PGM Total loading: 0.2 mg/$cm^2_{electrode}$
- Cost*: $ 30/kW_e
- Durability w/cycling (80°C): 5000 hrs

*based on Pt cost of $450/troy ounce

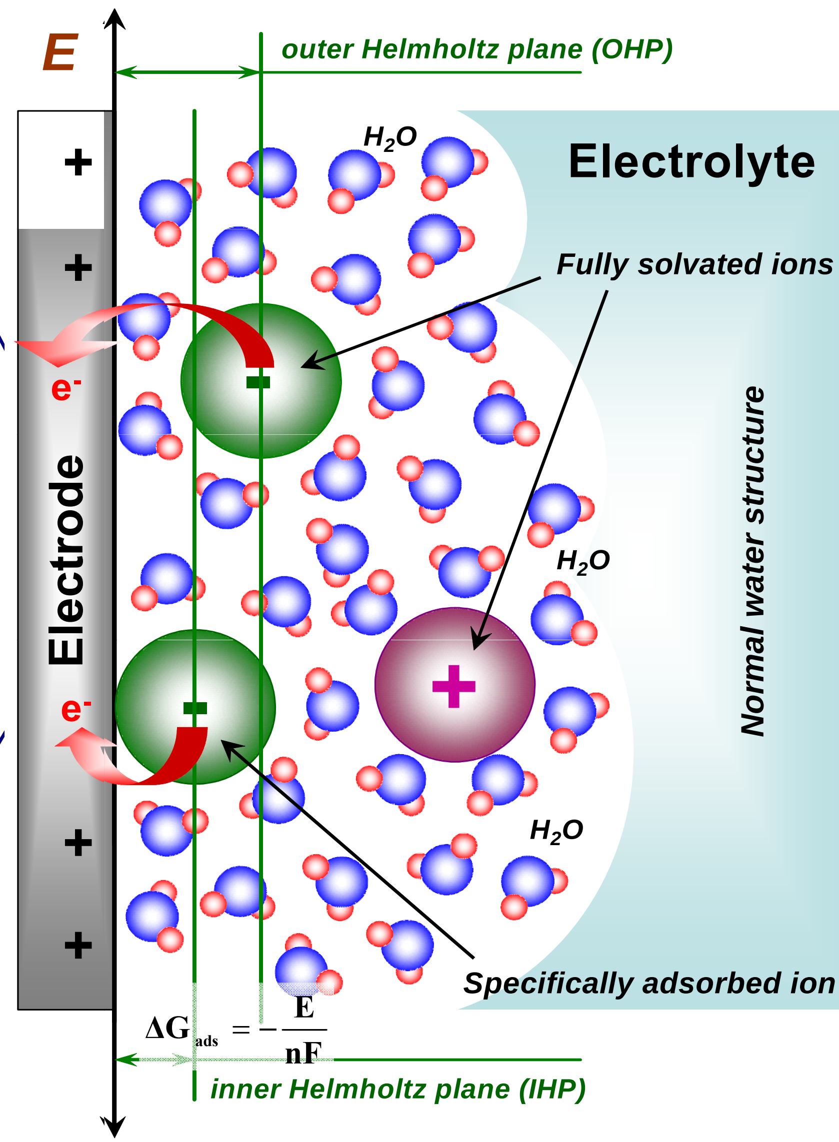


Main limitations in fuel cells:

1) **Activity:** Pt/C = Pt-poly/10
2) **Durability:** (Pt catalyst dissolves)
3) **High content of Pt:** Cost Issues

ELECTRIFIED SOLID-LIQUID INTERFACES

1. Reactants / Products
2. Electrode Material / Active Sites
3. Surface Structure — Surface Electronic Properties
4. (Sub)Surface Composition
5. NP Catalyst (Shape, Size, Support)
6. Electrolyte, Ions, pH, Impurities
7. Temperature [C]
8. Potential [V]
9. Activity, Stability, Selectivity



Activity | Durability | PGM Loading/Cost

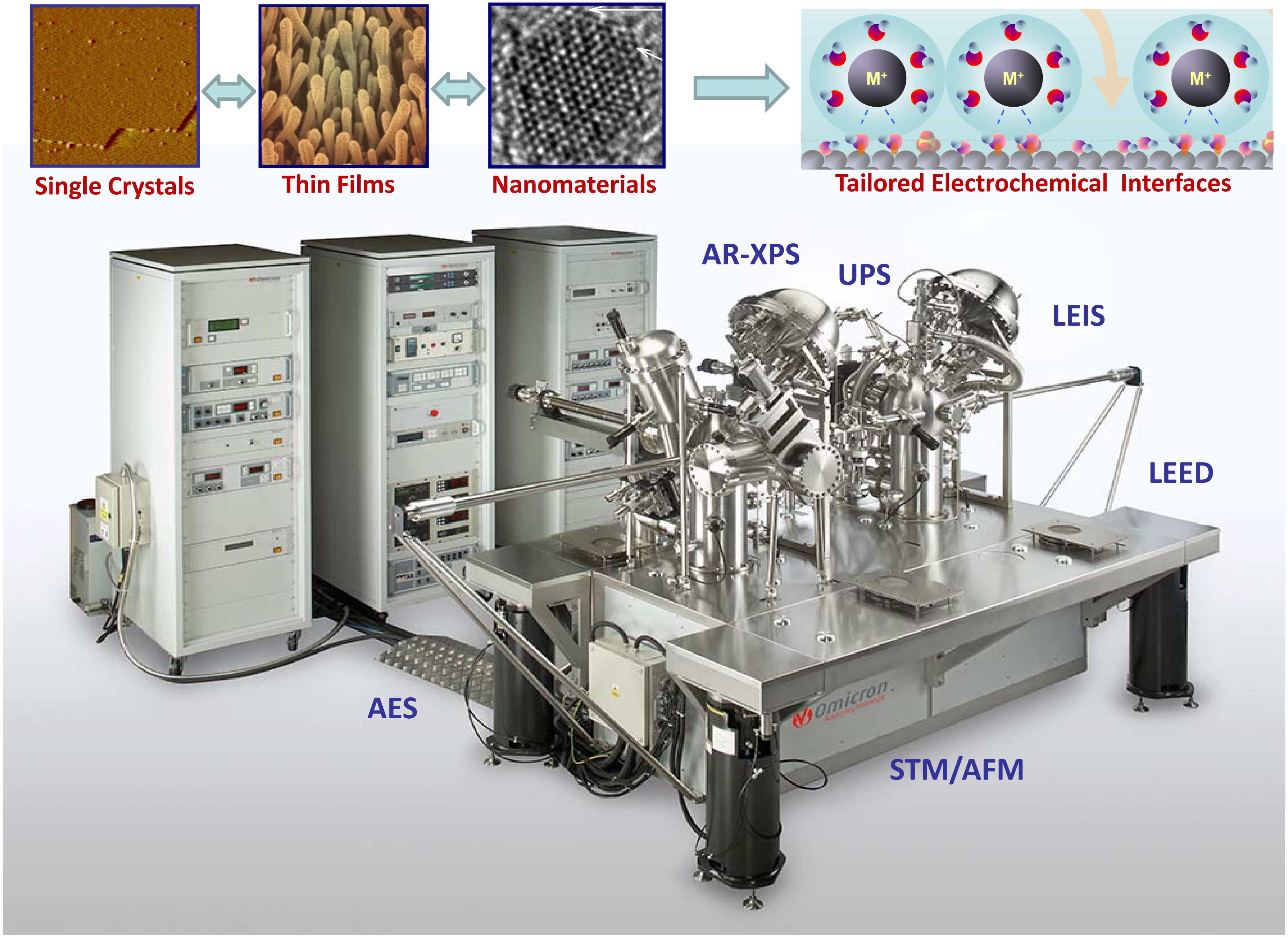
Specific Activity — Electrochemical Stability — Mass Activity

1° Surface Modifications

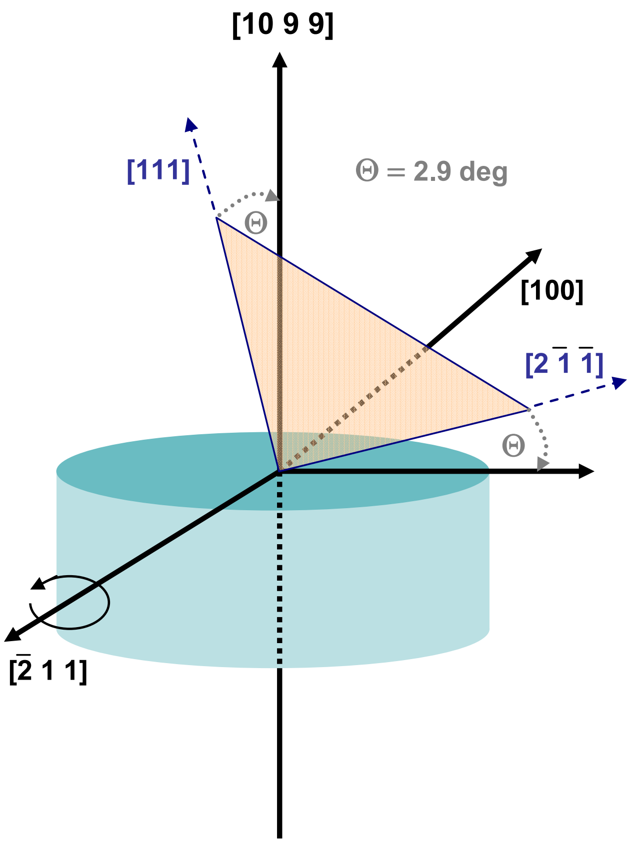
2° Tailored Electrolytes

3° Structure-Function

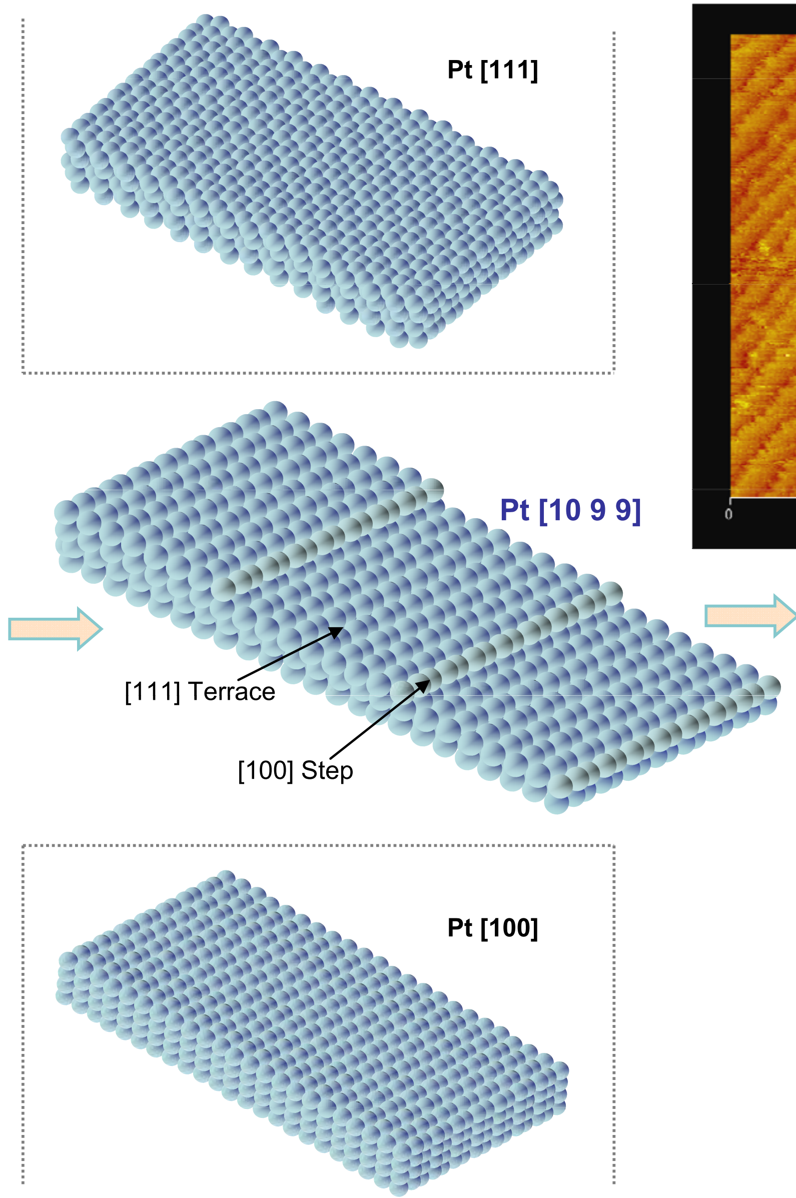
4° Composition-Function

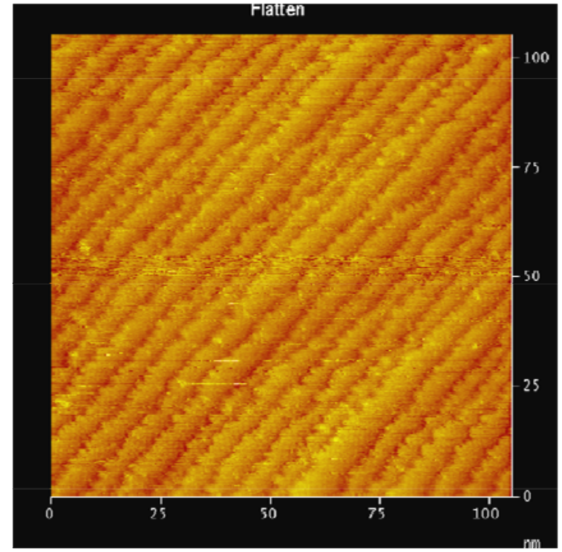

Single Crystals
Thin Films
Nanomaterials
M+
M+
M+
Tailored Electrochemical Interfaces
AR-XPS
UPS
LEIS
LEED
AES
STM/AFM
Omicron

Well-Defined Surfaces



Single Crystals



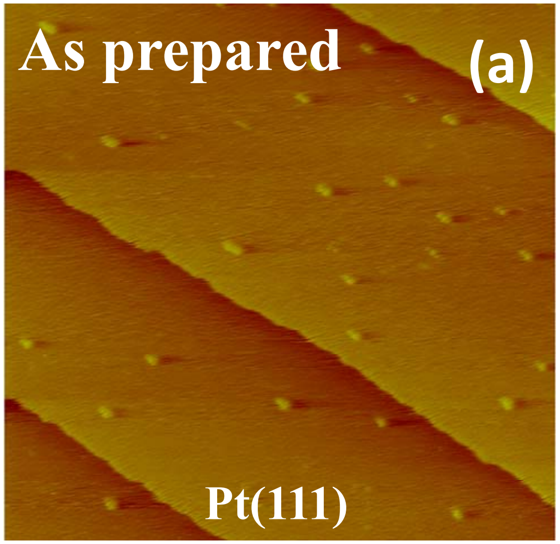


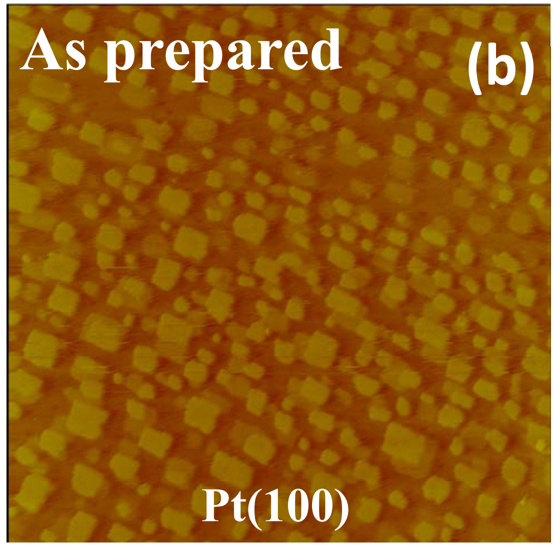
STM: Pt [10 9 9]

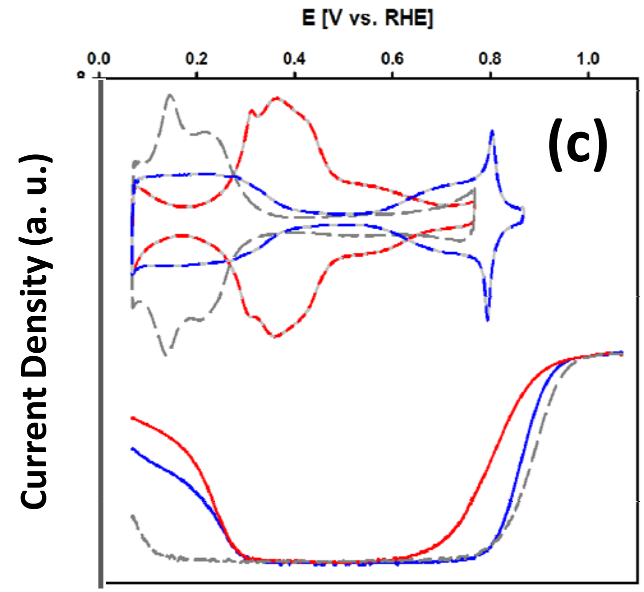
- **monoatomic steps**

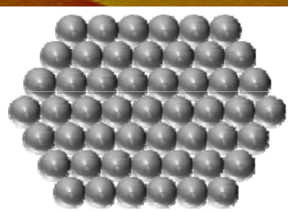
- **average terrace length: ~6nm**

Surface Structure and the ORR rate: *Pt Single Crystals*

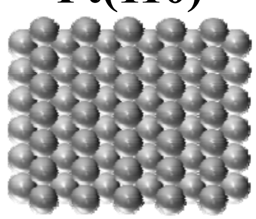


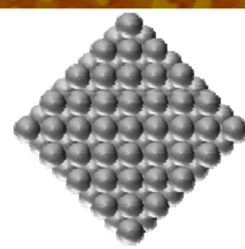


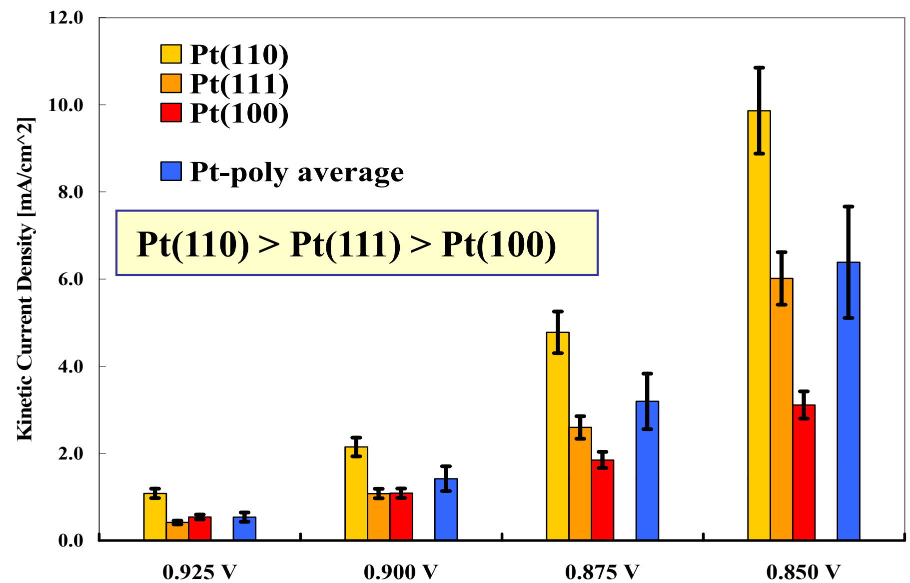




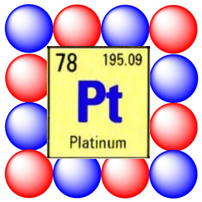
Pt(110)



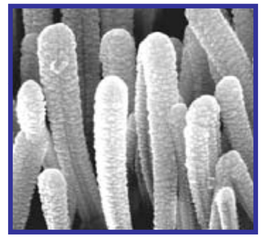




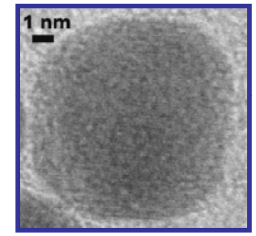
Pt Alloys



BULK SINGLE CRYSTALS



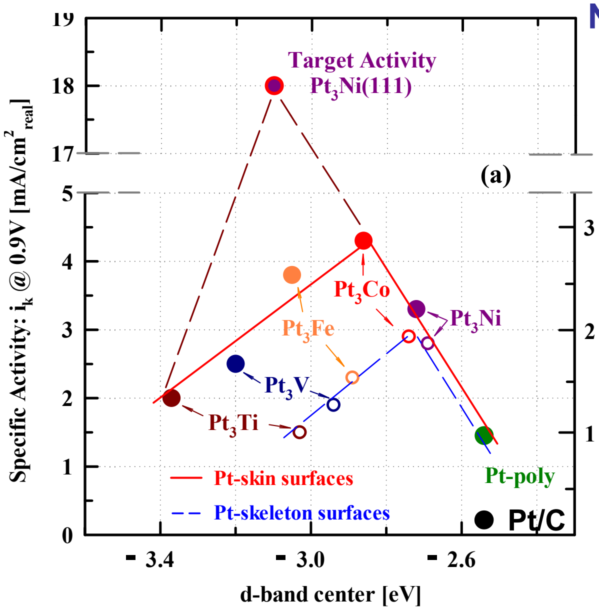
THIN METAL FILMS



NANOPARTICLES

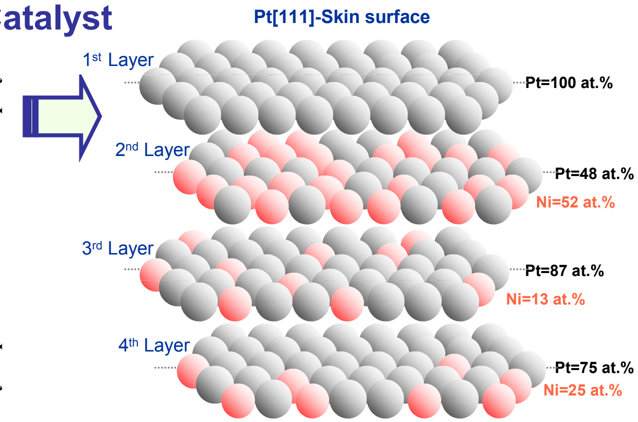
Materials-by-design approach - developed by ANL to design, characterize, understand, synthesize/fabricate and test advanced nanosegregated multi-metallic nanoparticles and thin metal films

Well-Defined Systems



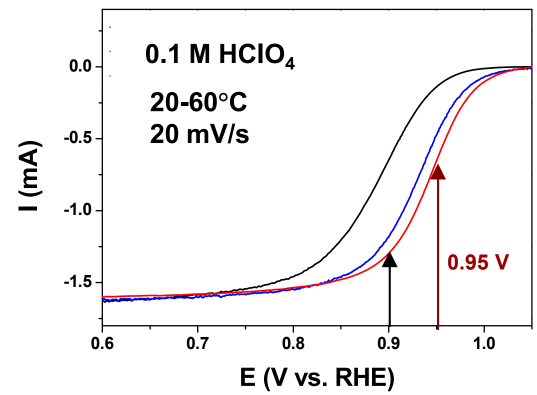
Advanced Nanoscale Catalyst

Nanosegregated Profile



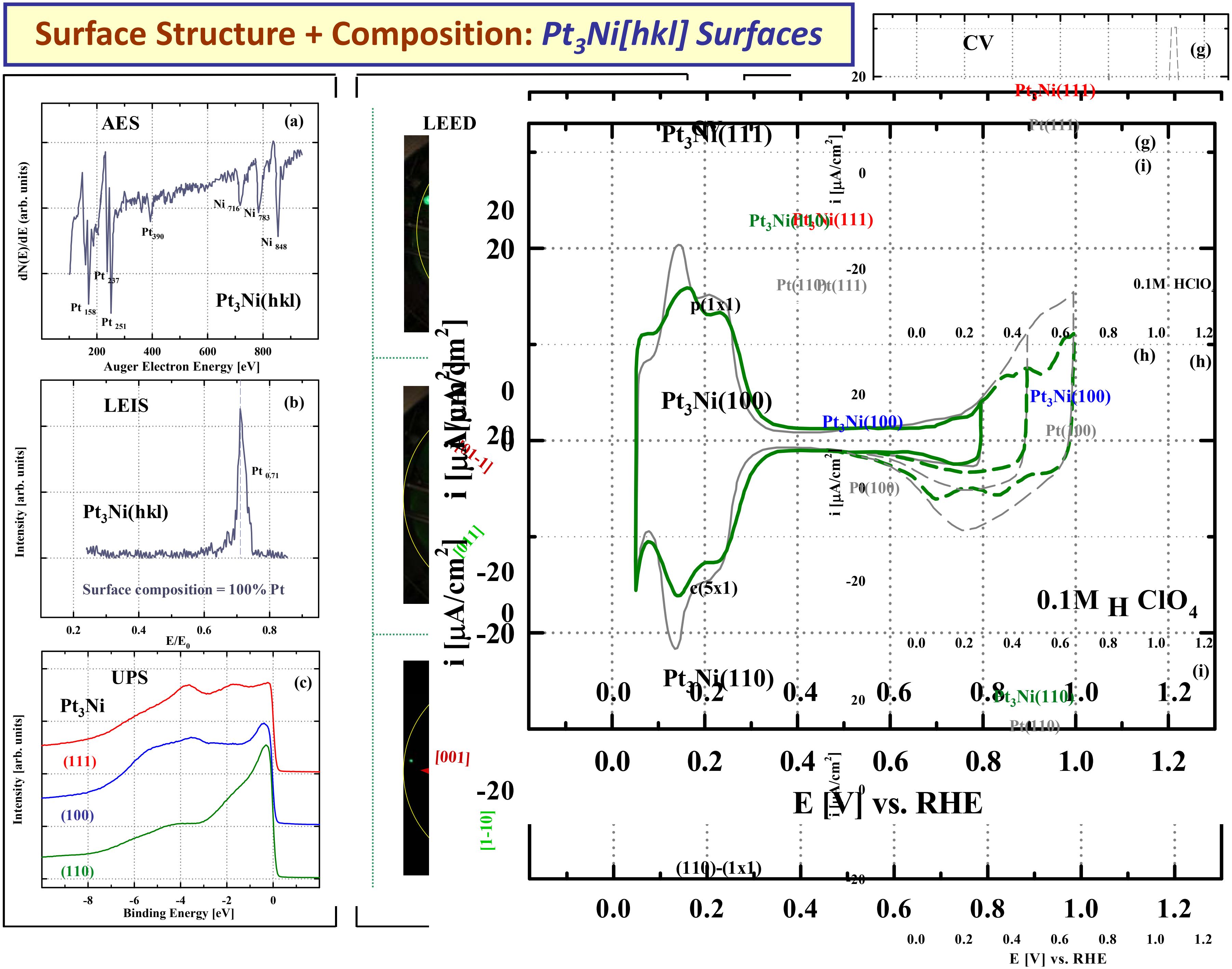
$Pt_3Ni(111)$-Skin ~100 times more active than the state-of-the-art Pt/C catalysts

Intrinsic Activity



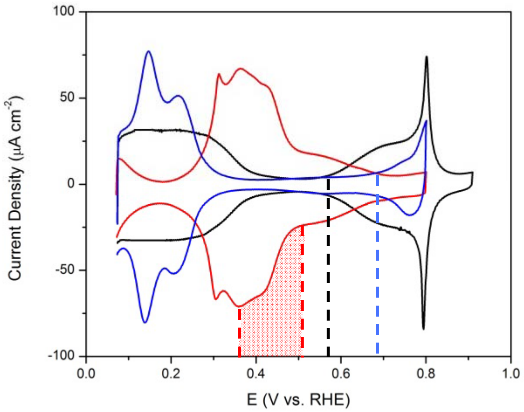
RDE:
- ORR activity measured at 0.95V
- iR corrected currents
- Measurements without ionomer

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

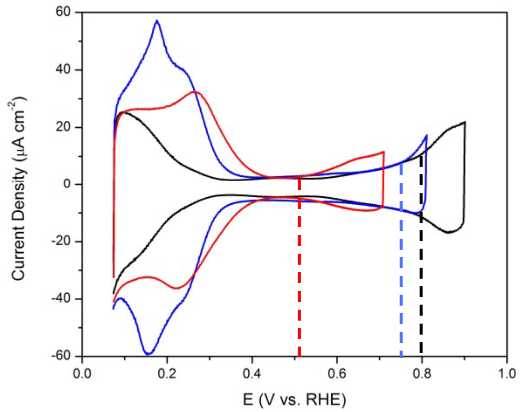


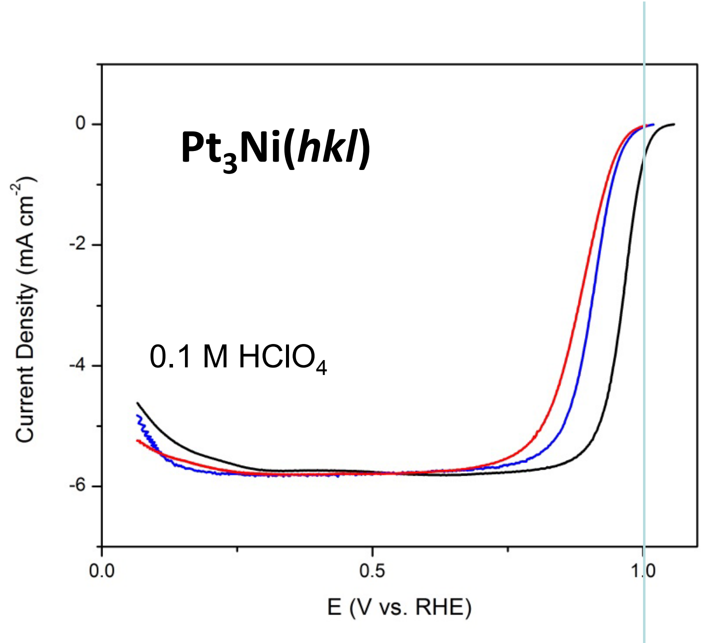
Activity: *ORR Platinum Alloy Surfaces*

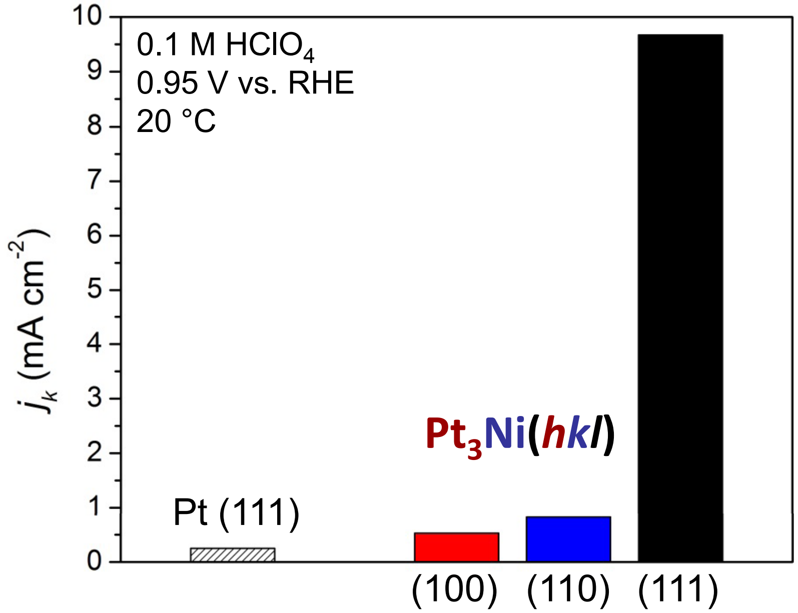
Pt(*hkl*)

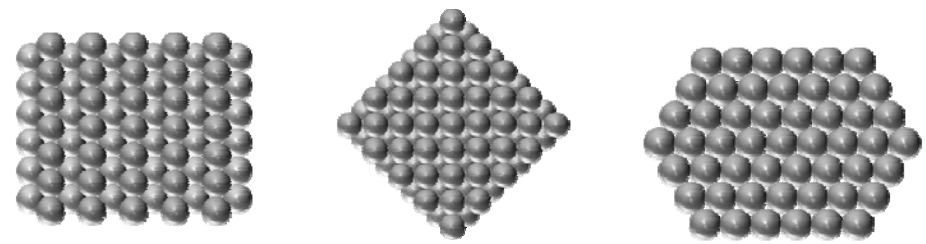


Pt_3Ni(*hkl*)





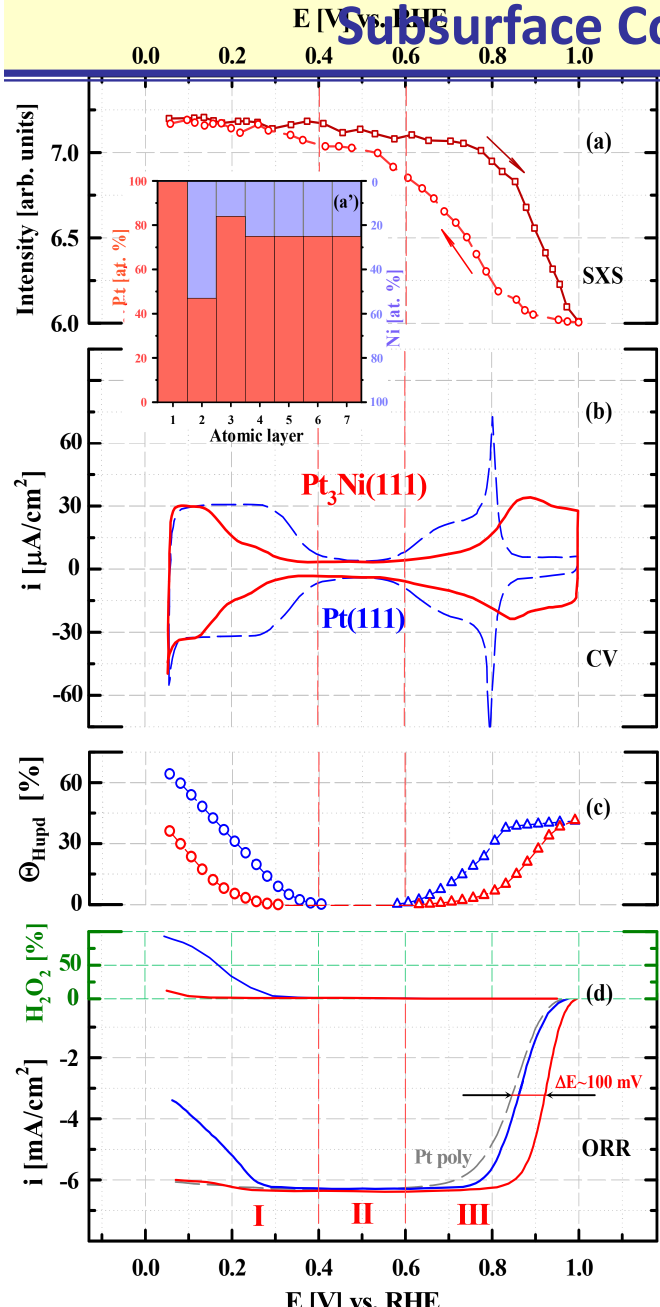




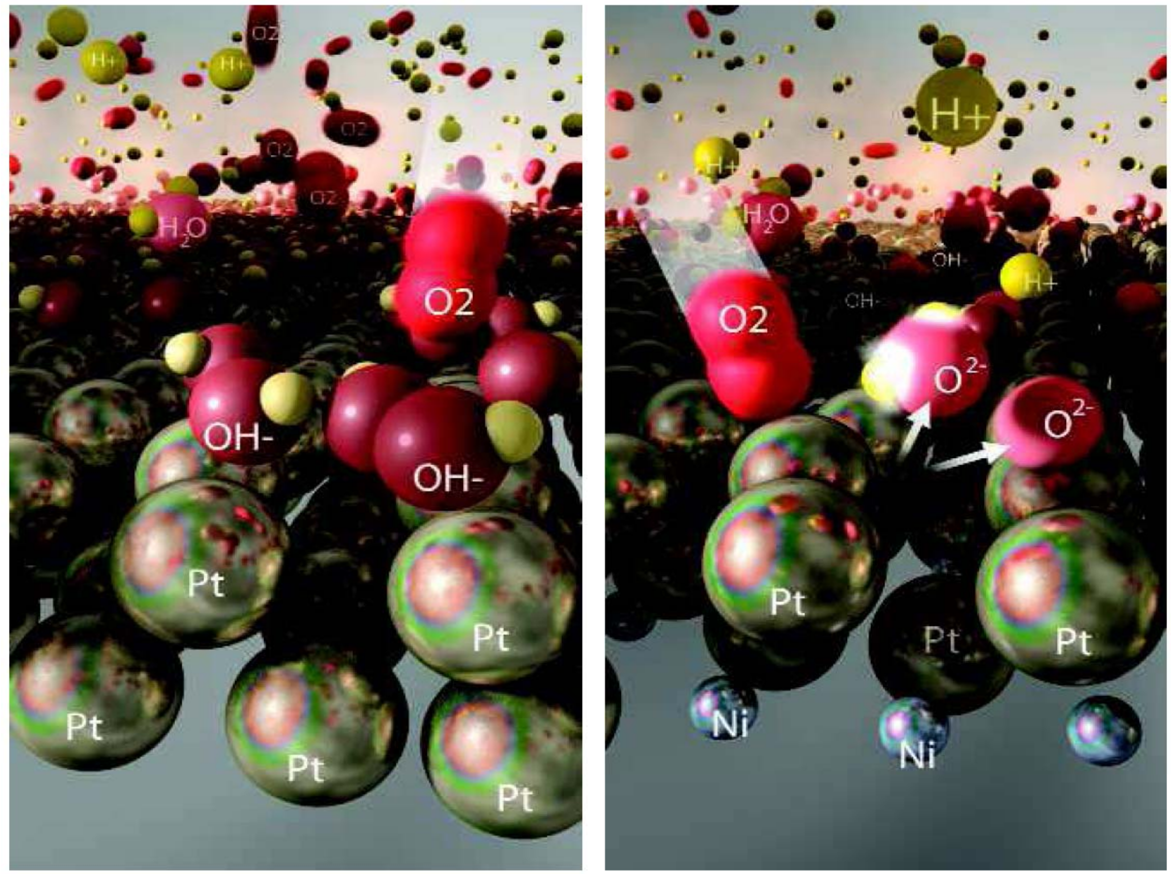
$Pt_3Ni(111)$/Pt-Skin Surface is the most active catalyst for the ORR (100-fold enhancement)

Science, *315 (2007) 493*

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



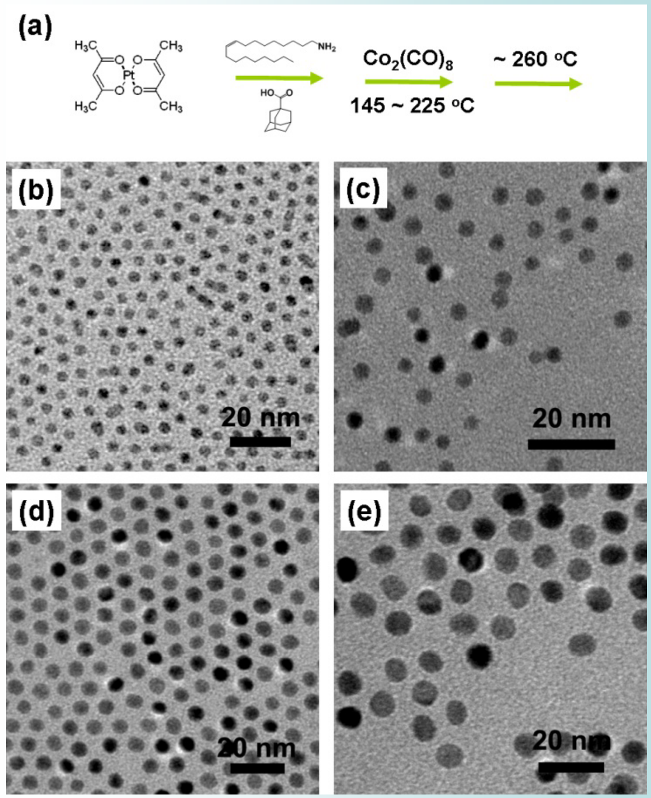
Segregation Profile



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

Pt-alloy Catalysts

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



Efficient surfactant removal method does not change the catalyst properties

1º Particle size effect applies to Pt-bimetallic NPs

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

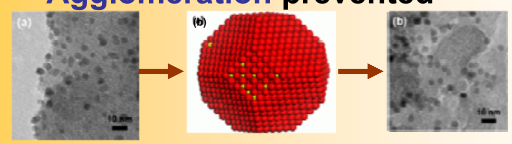
Mass Activity decreases with particle size

Optimal size particle size ~5nm

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

2º Temperature induced segregation in Pt-bimetallic NPs

Agglomeration prevented

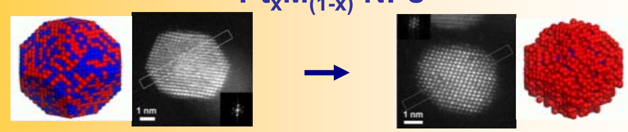


Optimized annealing temperature 400-500ºC

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

3º Surface chemistry of homogeneous Pt-bimetallic NPs

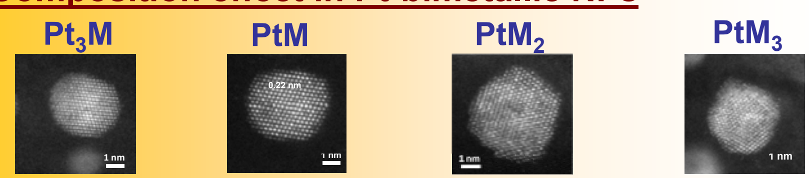
$Pt_xM_{(1-x)}$ NPs



Dissolution of non Pt surface atoms leads to **Pt-skeleton** formation

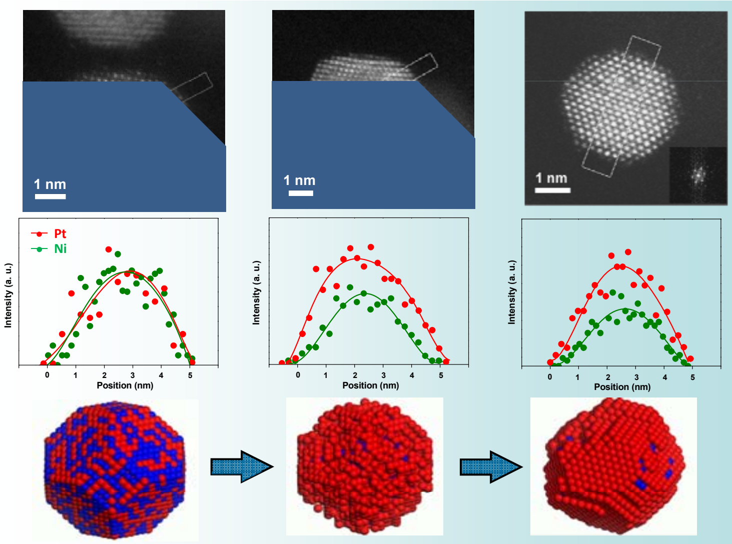
Adv. Funct. Mat., 21 (2011) 14715

4º Composition effect in Pt-bimetallic NPs



Optimal composition of Pt-bimetallic NPs is PtM

Pt-alloy Catalysts



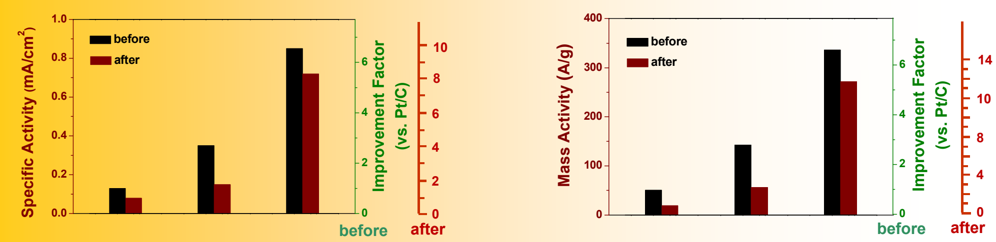
JACS 133 (2011) 14396

5° Pt-bimetallic catalysts with mutilayered Pt-skin surfaces

Synthesized PtNi NPs have homogeneous distribution of Pt, Ni

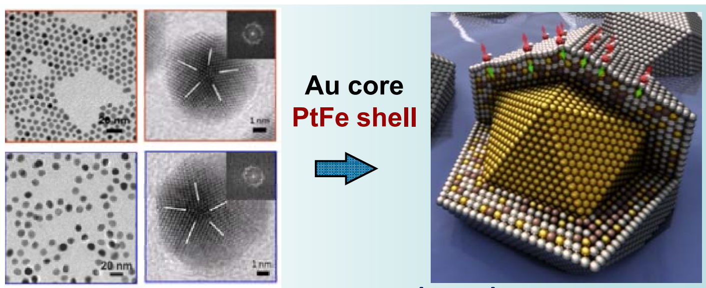
3-4ML of Pt-skeleton surfaces for PtNi acid leached NPs

Multilayered Pt-skin surfaces confirmed for PtNi annealed NPs

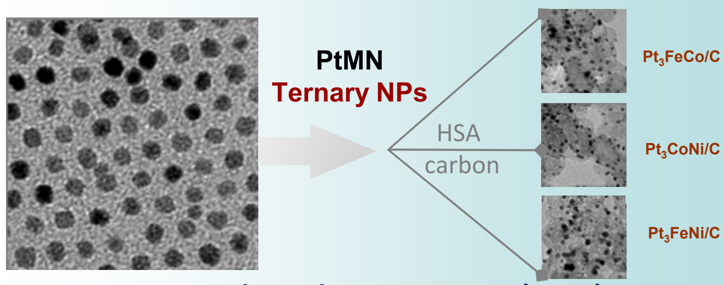


RDE after 4K cycles @60°C (0.6-1.05V vs. RHE):

8-fold specific and 10-fold mass activity improvements over Pt/C

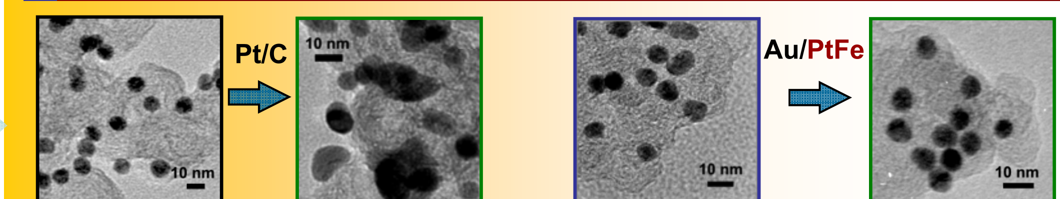


Nano Letters, 11 (2011) 919

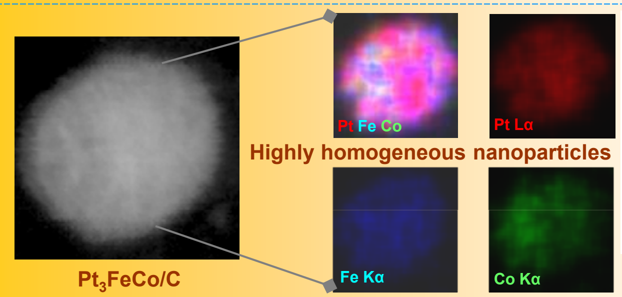


J. Phys. Chem. Letters, 3 (2012) 1668

6° Multimetallic NPs can further improve activity and durability

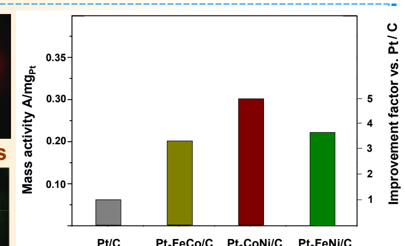


before | After 60K cycles | before | After 60K cycles



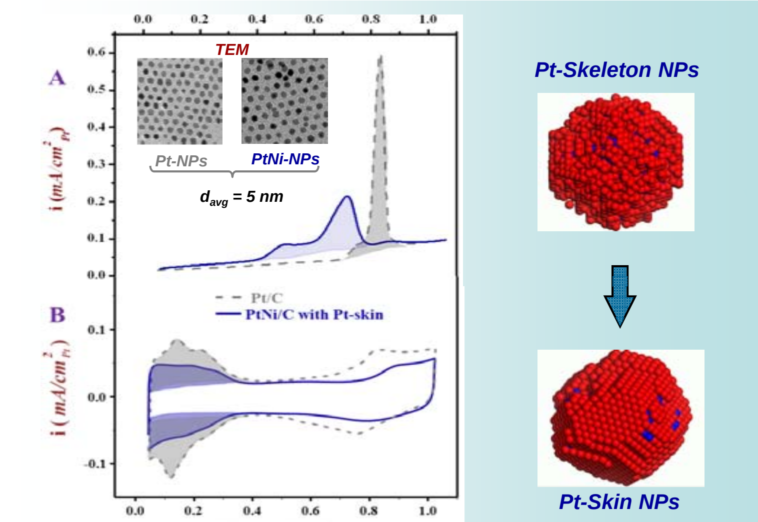
Highly homogeneous nanoparticles

Pt_3FeCo/C



Additional gain in mass and specific activities vs. Pt and Pt_3M alloys

Technical Accomplishments FY09-12: *Pt-alloy Nanocatalysts*



Agewandte Chemie 51 (2012) 3139

7° Electrochemically active surface area of Pt-Skin catalysts

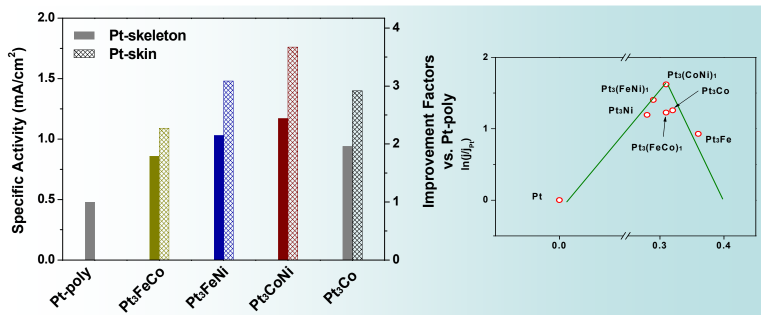
Catalysts with multilayered Pt-skin surfaces exhibit substantially lower coverage by H_{upd} vs. Pt/C (up to 40% lower H_{upd} region is obtained on Pt-Skin catalyst)

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

Electrochemical oxidation of adsorbed CO should be used for estimation of EAS of Pt-skin catalysts

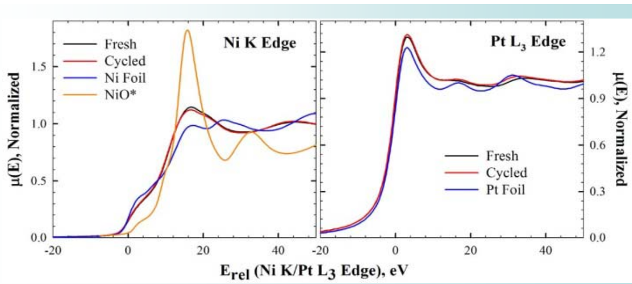
Benefits: to avoid overestimation of specific activity



8° Multimetallic Pt_3NM alloys can further improve activity

Similarly to Pt_3M alloys, ternary alloys form Pt-skeleton and Pt-skin surfaces depending on the surface treatment

The most active alloy is Pt_3NiCo, with 4-fold improvement factor in specific activity compared to Pt-poly

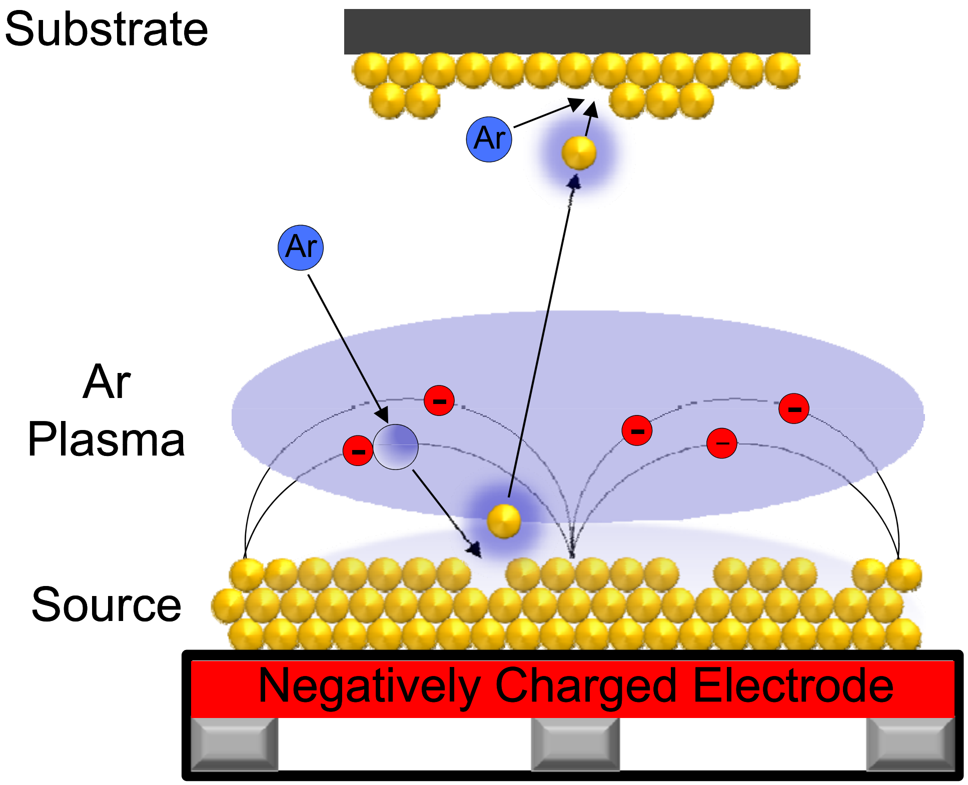


9° MEA: PtNi-MLSkin/NPs 20,000 potential cycles, 0.6 – 0.95 V

No change in Ni and Pt edges after 20K cycles confirms high stability pf multilayered Pt-Skin under operating conditions

Specific surface area loss was only 12%, while Pt/C catalysts suffer loss of 20-50%

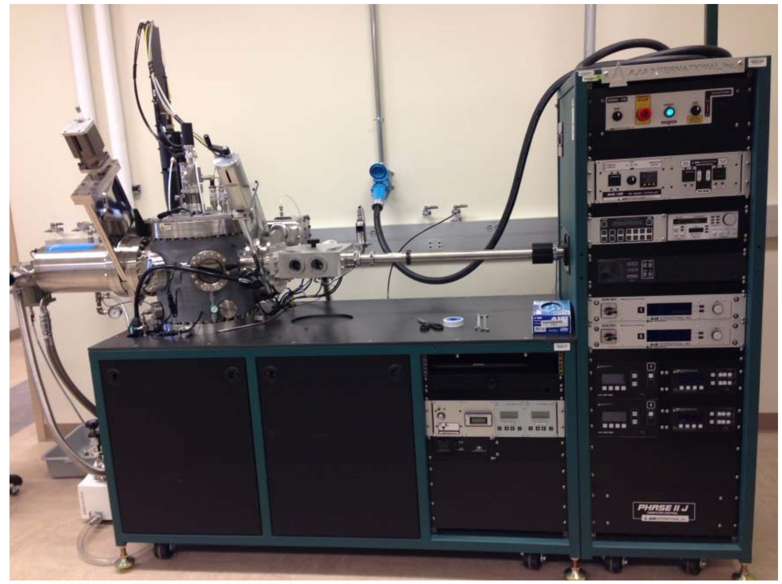
Magnetron Sputter Deposition



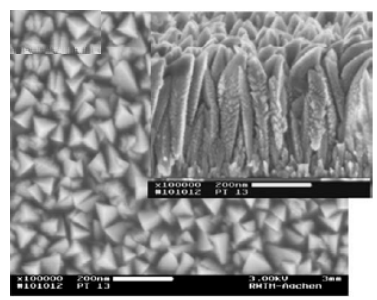
Variable Parameters:

- substrate temperature
- source power
- type of source power: RF or DC
- type of ionizing process gas
- process gas pressure
- substrate bias

Ultra High Vacuum (UHV)
Base pressure: 10^{-10} torr

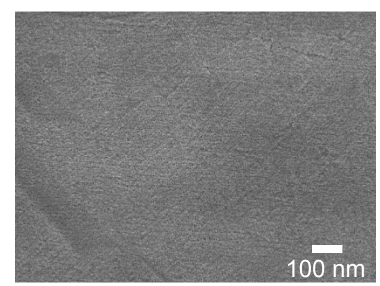


Low density film

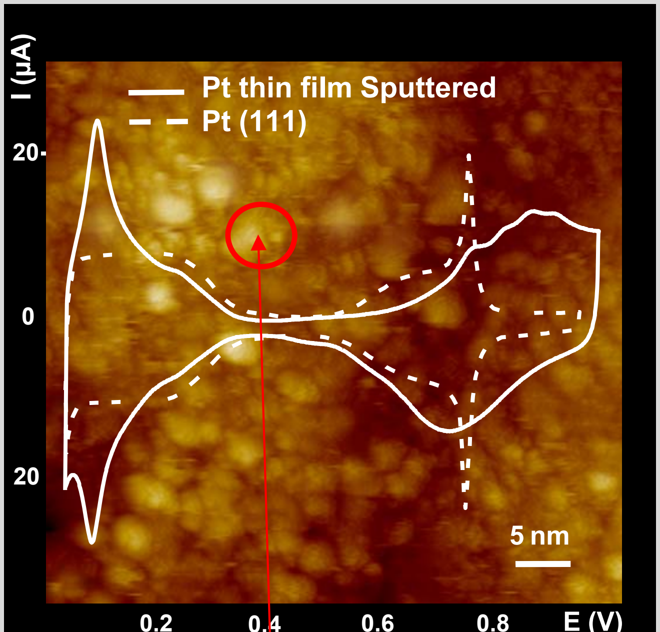


Appl. Surf. Sci. 255 (2009) 6479

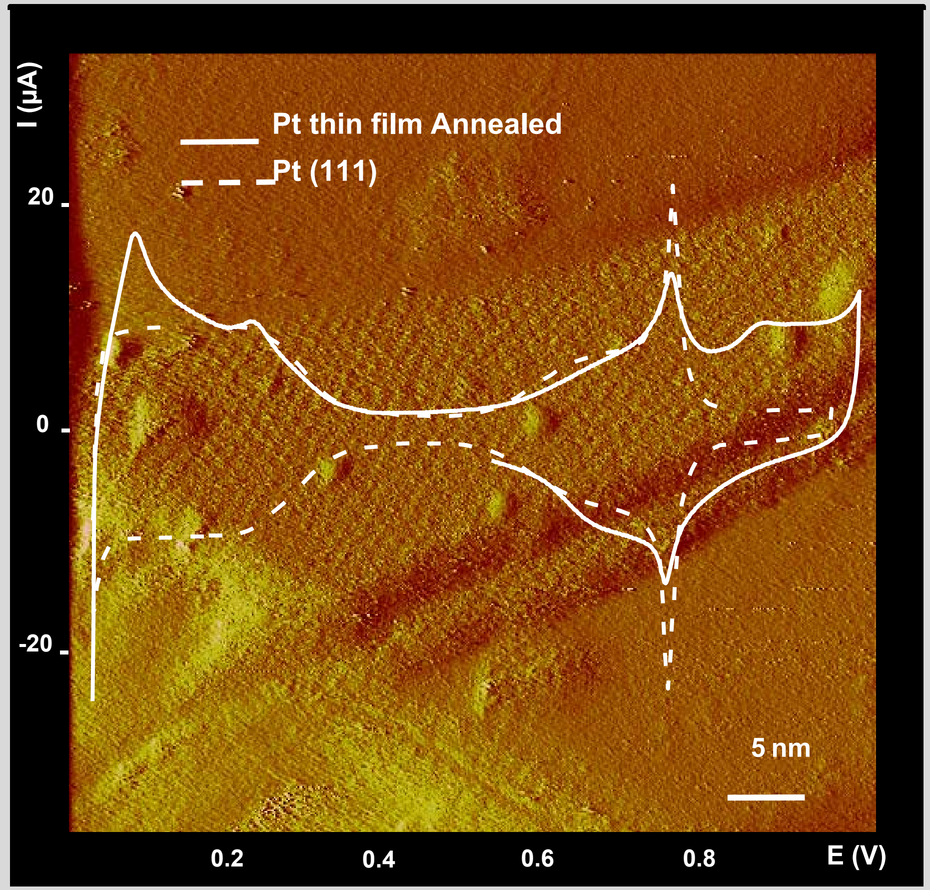
High density film



Tailoring Surface Structure: *Pt-Thin Films*



ΔT



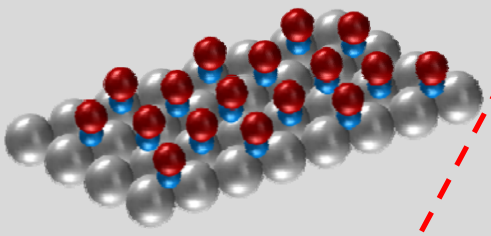
~5 nm grains

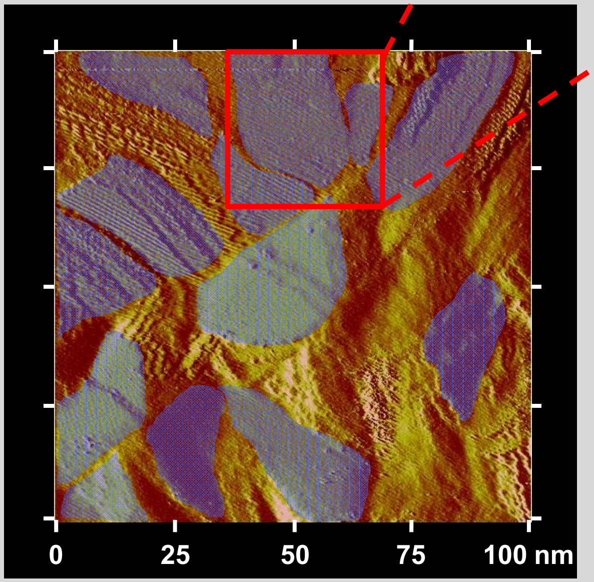
- Magnetron Sputtering Deposition
- Glassy Carbon Support

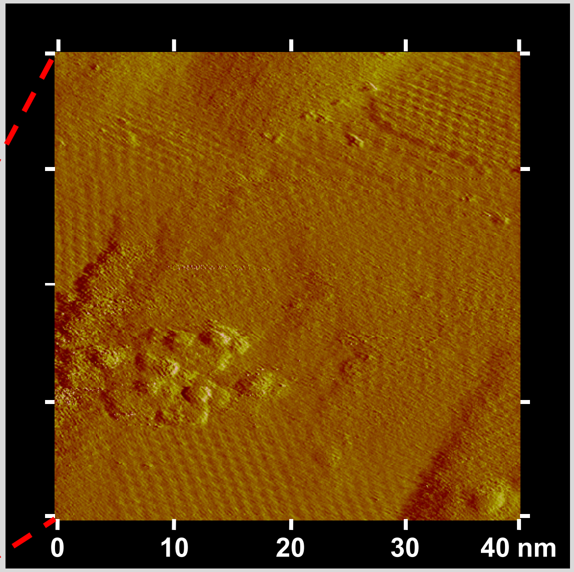
Tailoring Surface Structure: *Annealed Thin Films*

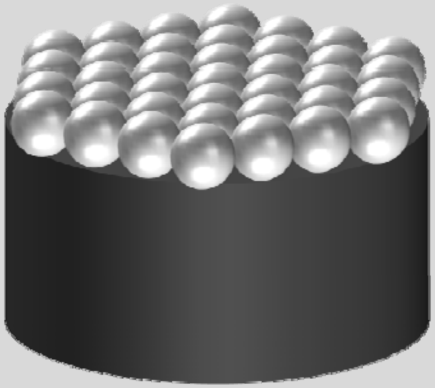
STM → Local atomic structure

$(2 \times 2) - 3CO$

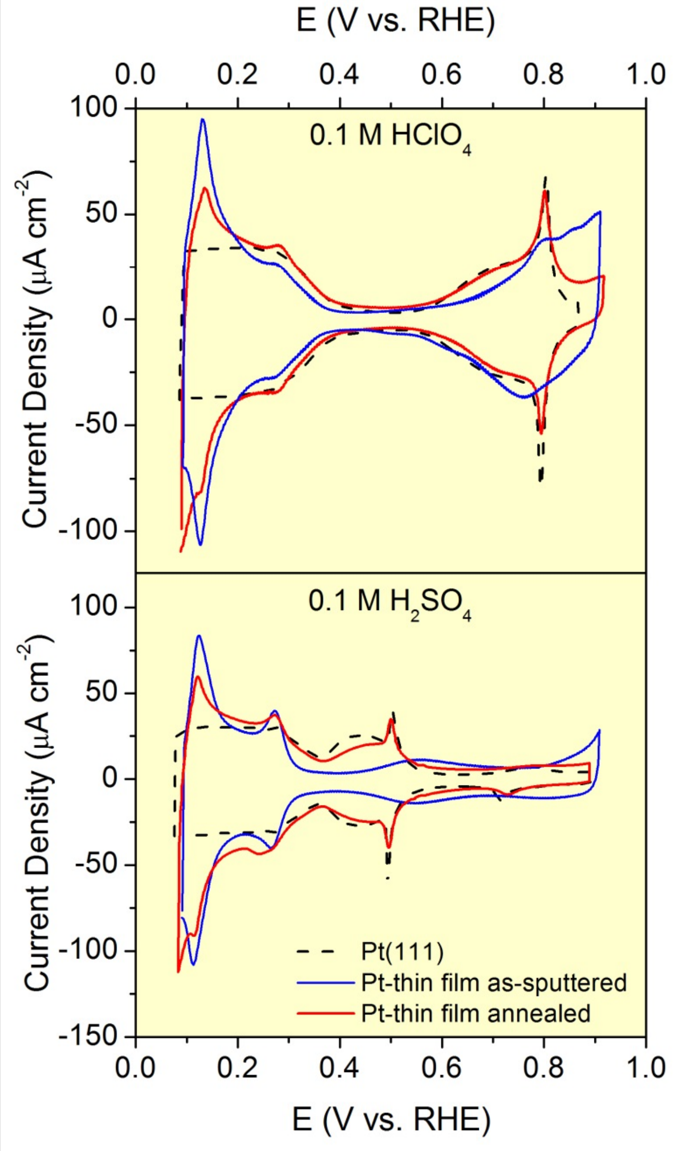






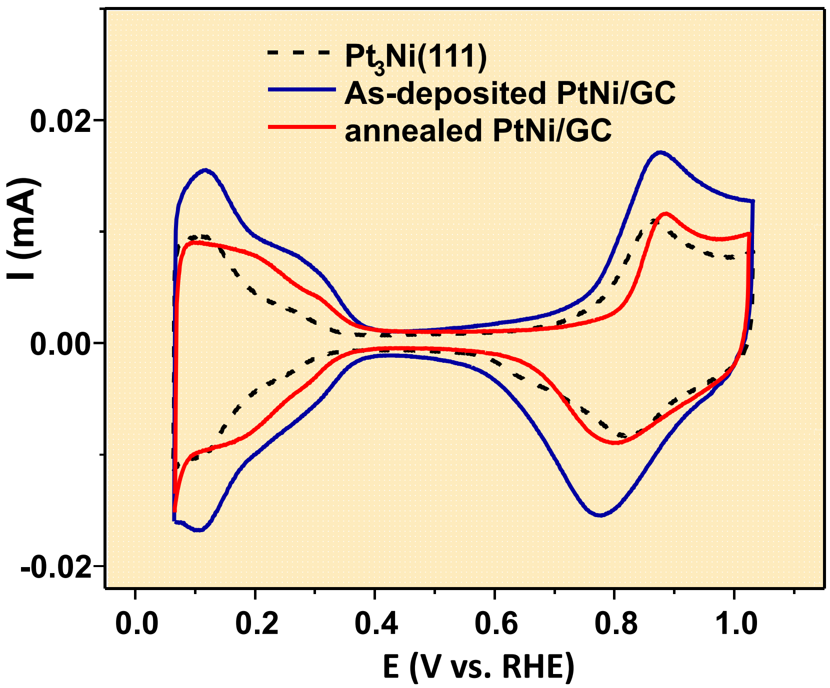


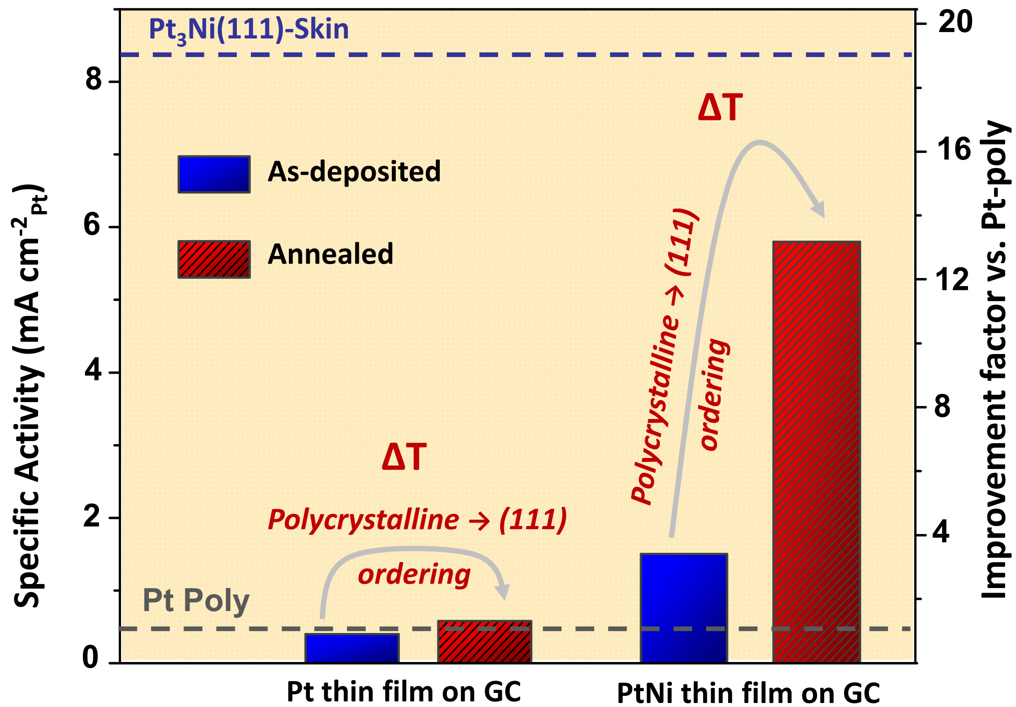
Amorphous Support glassy carbon



J. Phys. Chem. C 117(2013) 23790

Tailoring Structure and Composition: *Pt-Bimetalic Thin Films*

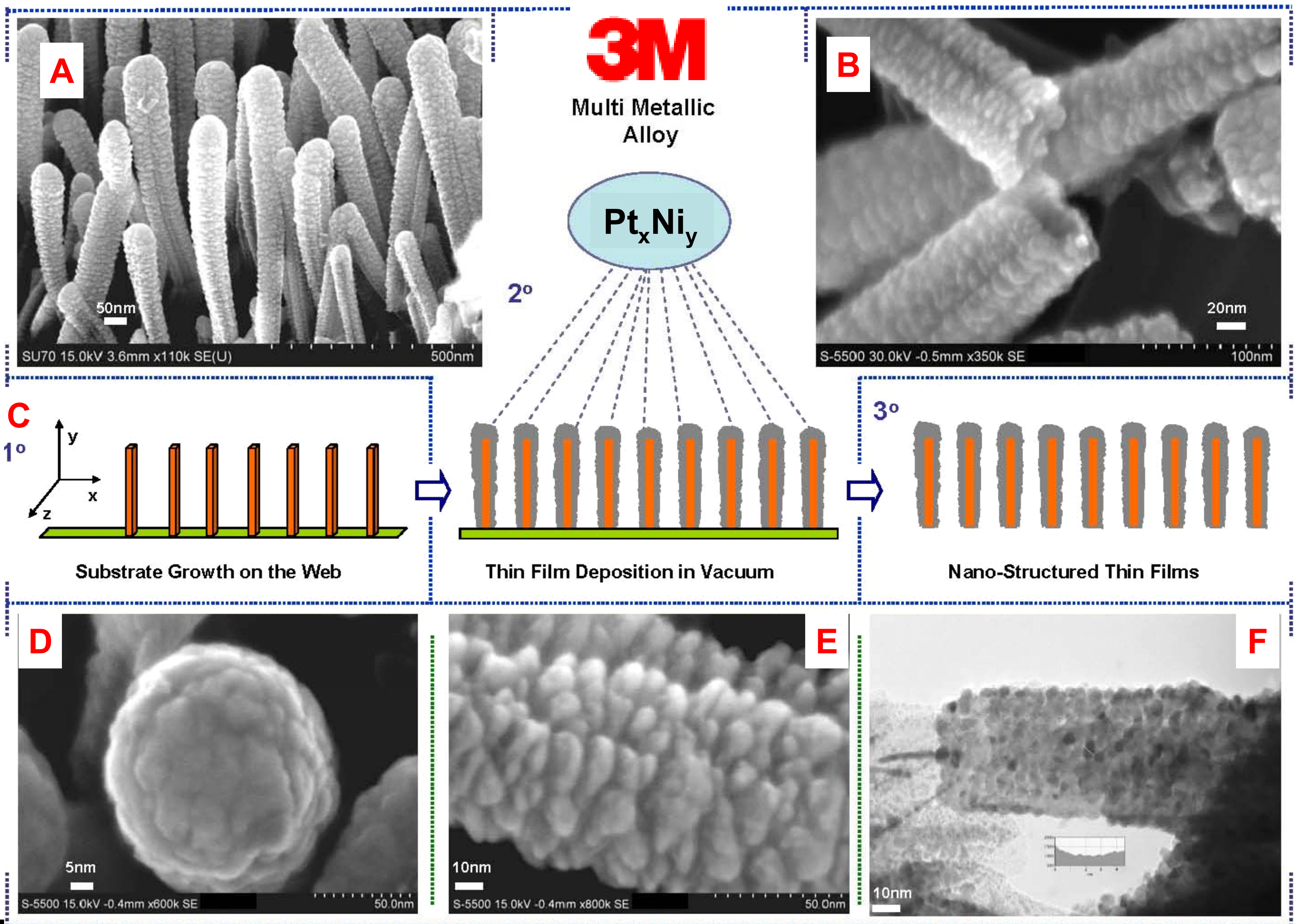




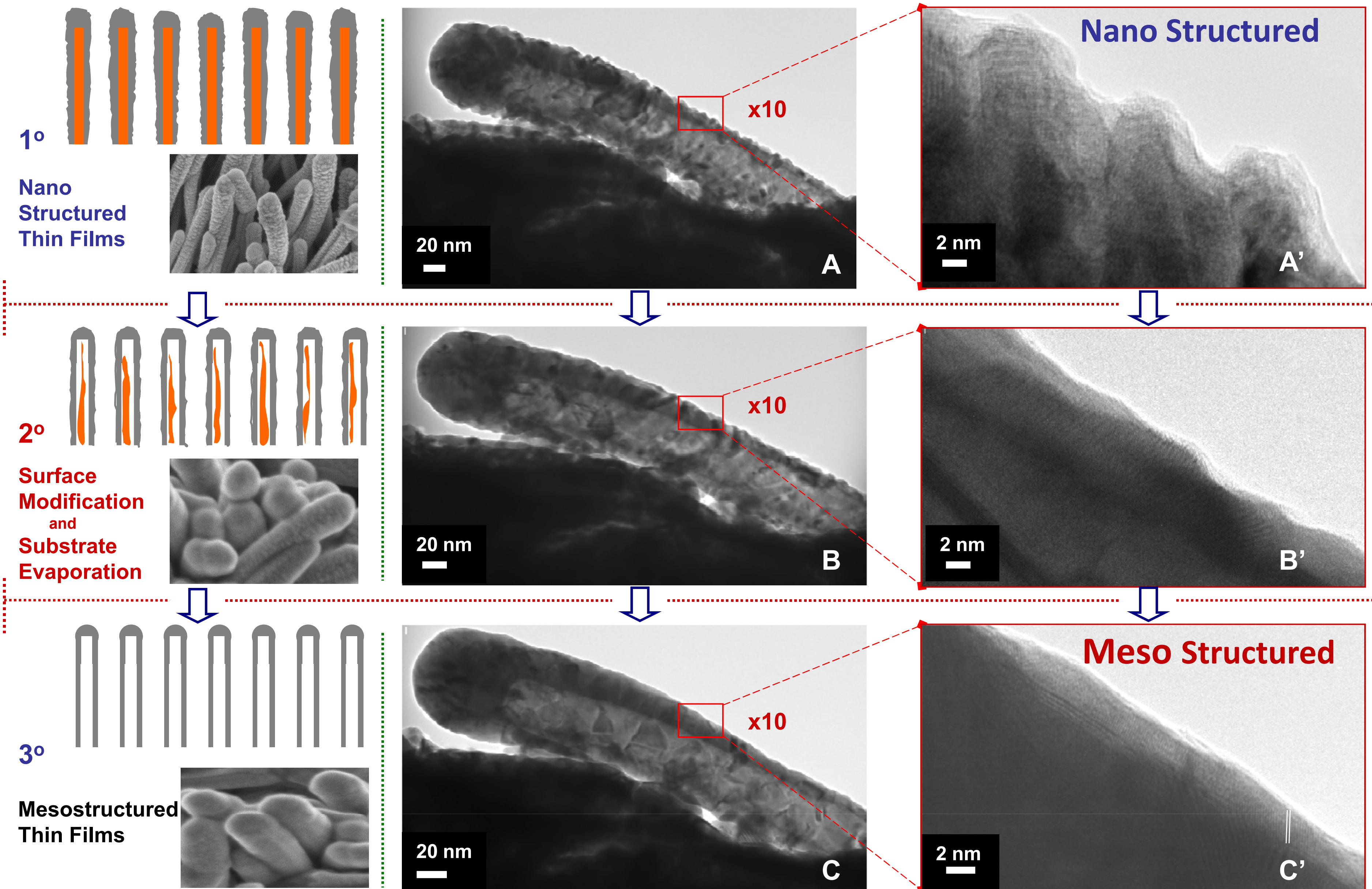
- RDE
- ORR @ 0.95V vs. RHE

MSTF vs. Pt/C:
SA 20-fold
MA 6-fold

High Resolution SEM: *NSTF Surface Morphology at Nanoscale*

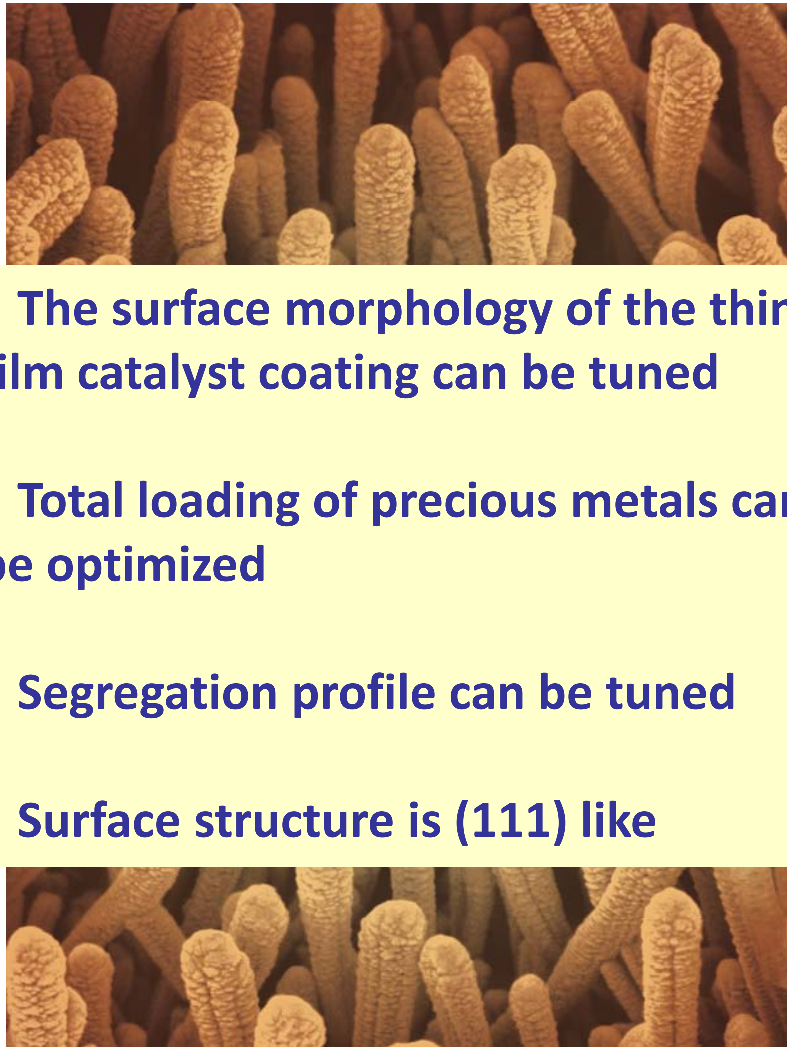


NSTF: *Tuning of the Thin Film Surface Morphology*

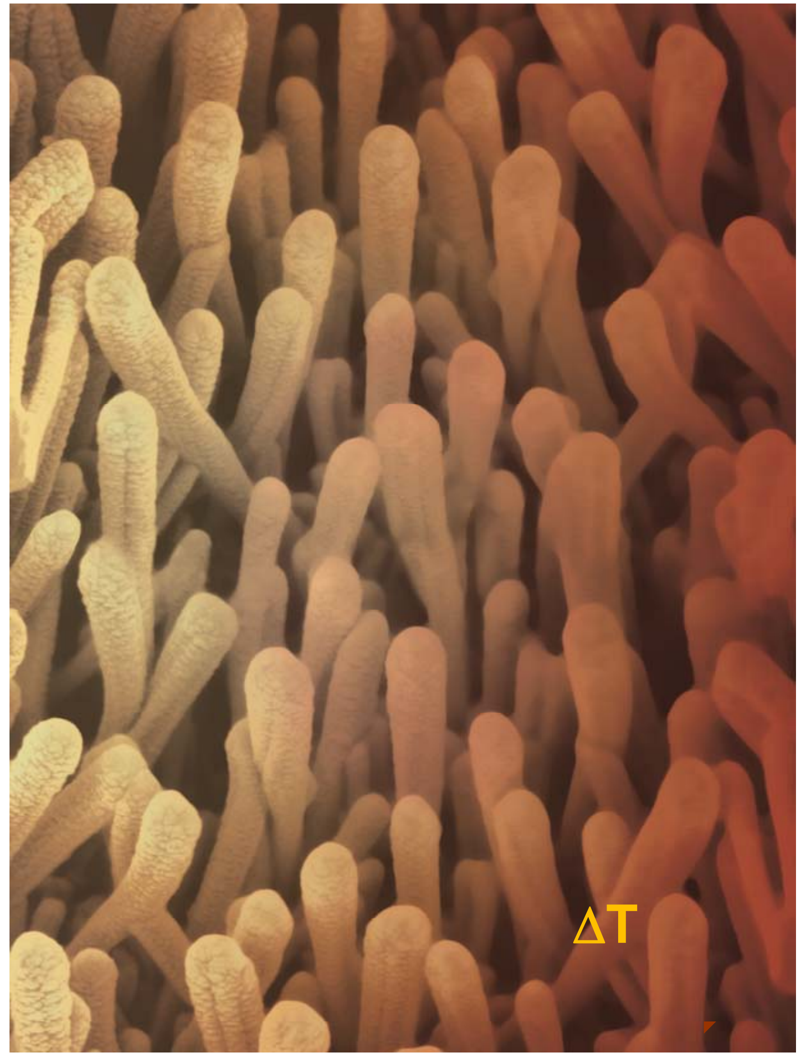


Tailored thin Film Electrocatalysts: *MSTF*

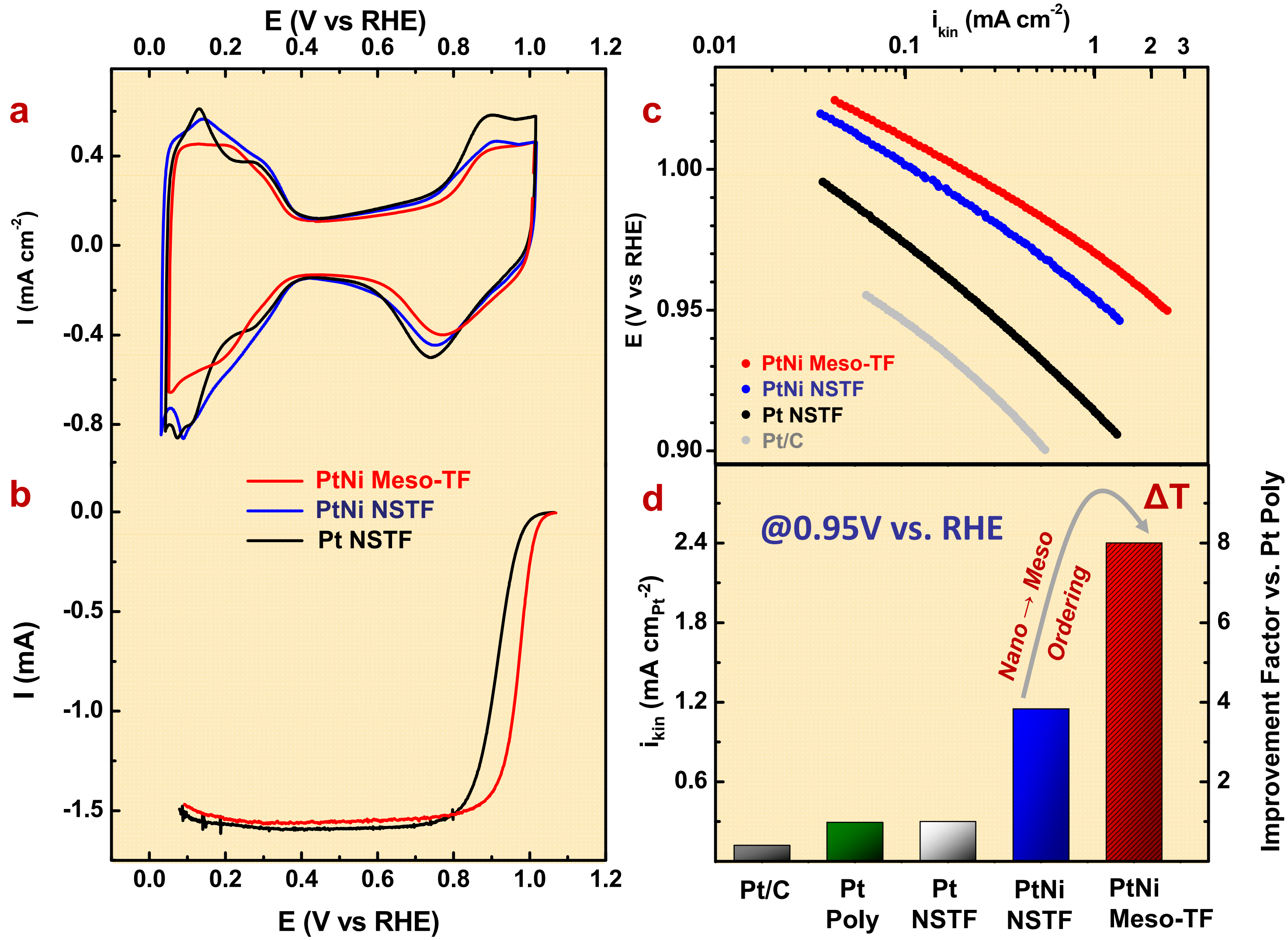
Nano-Structured → **Meso-Structured**



- The surface morphology of the thin film catalyst coating can be tuned
- Total loading of precious metals can be optimized
- Segregation profile can be tuned
- Surface structure is (111) like

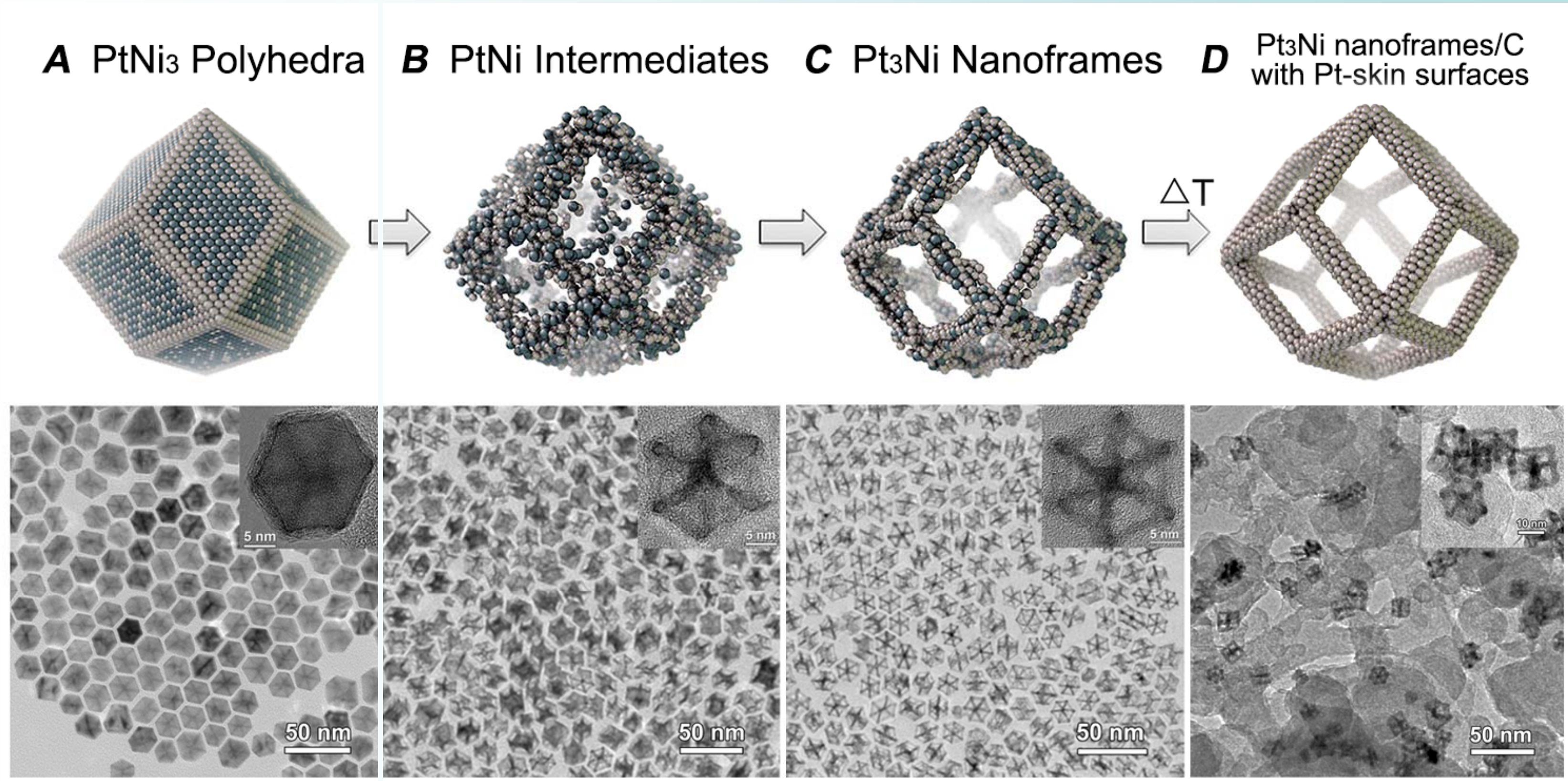


Electrochemical Characterization of MSTF by RDE



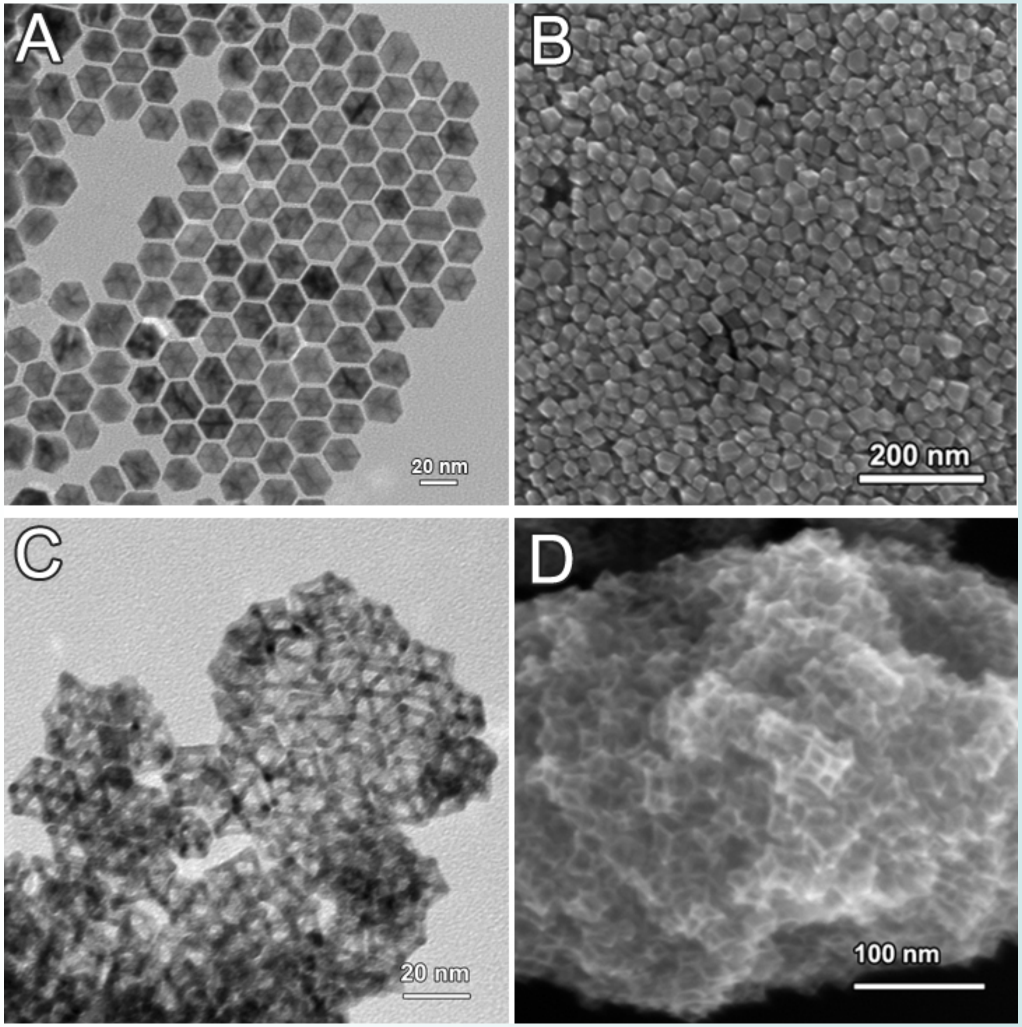
Tailoring Nanoarchitecture: *Multimetallic Nanoframes*

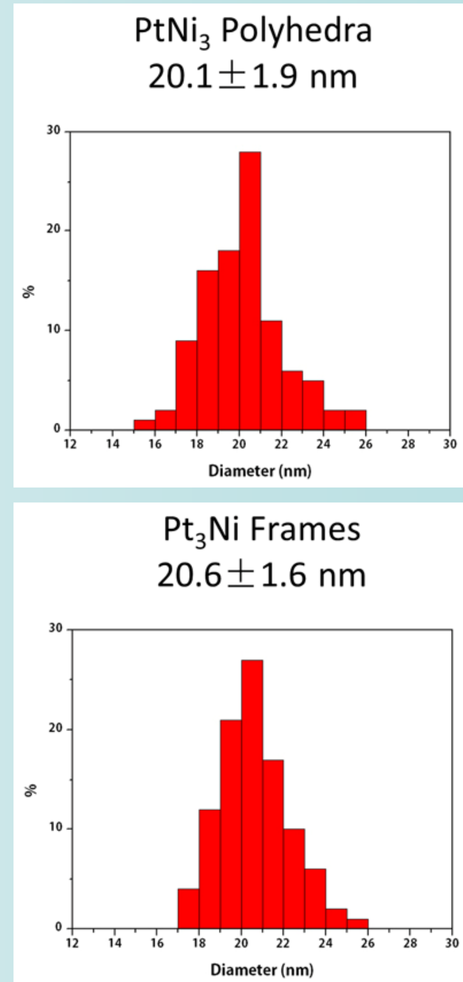
In collaboration with Peidong Yang, UC Berkeley



- 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

PtNi Nanoframes: *size distribution*

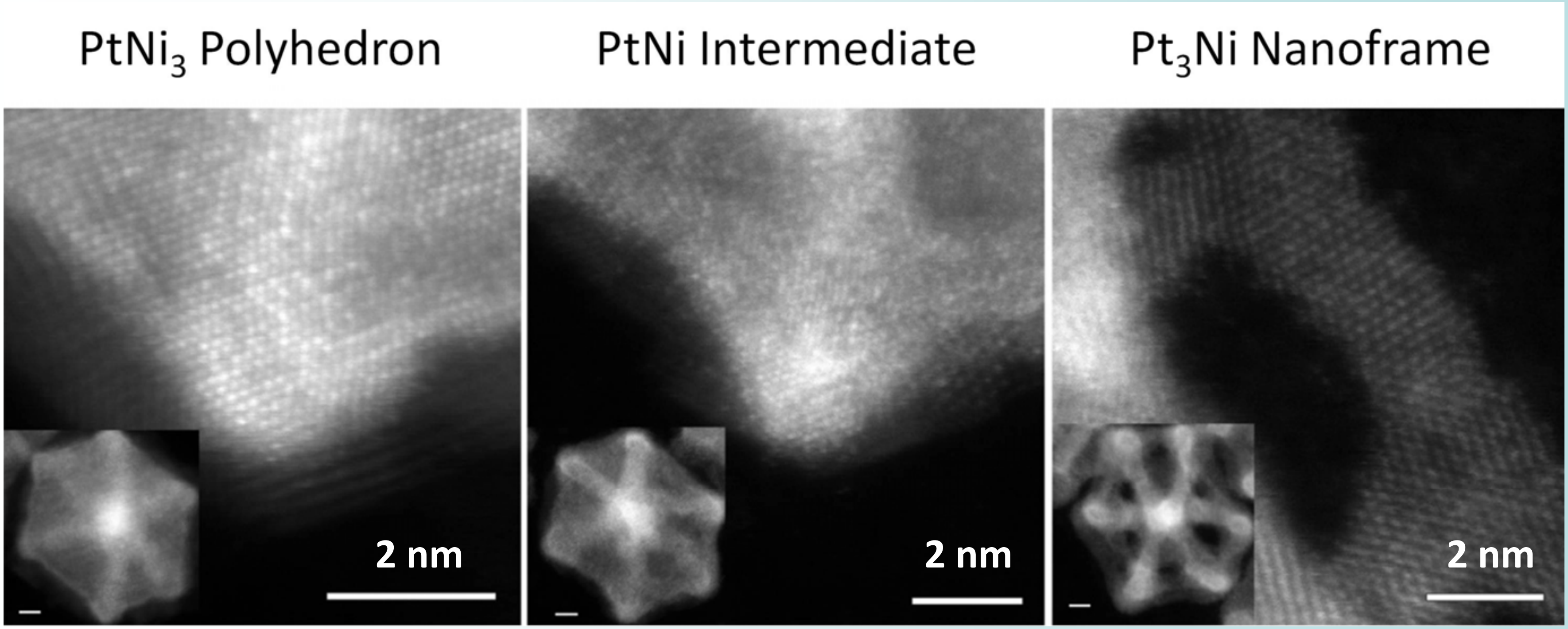




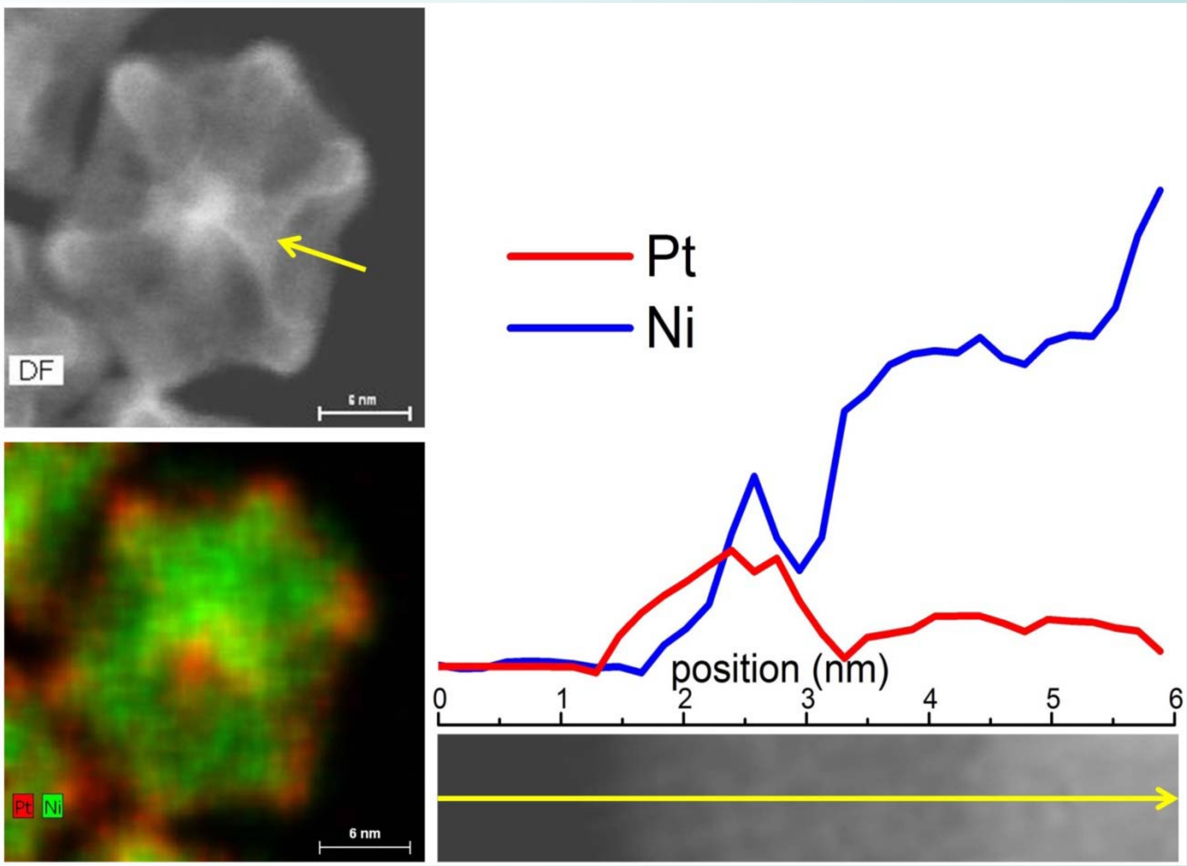
(A) TEM and (B) SEM images of parent $PtNi_3$ polyhedra. (C) TEM and (D) SEM images of Pt_3Ni nanoframes yielded after 2 weeks under ambient conditions

PtNi Nanoframes: *size, shape, crystallinity*

In collaboration with Karren More, ORNL

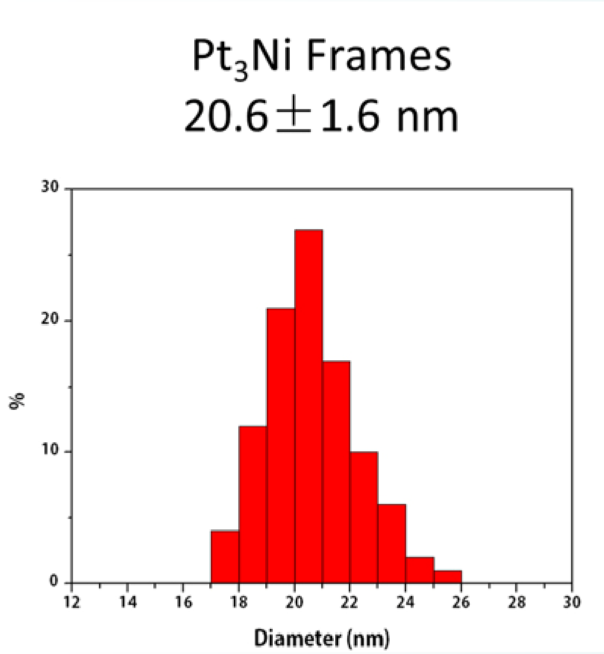


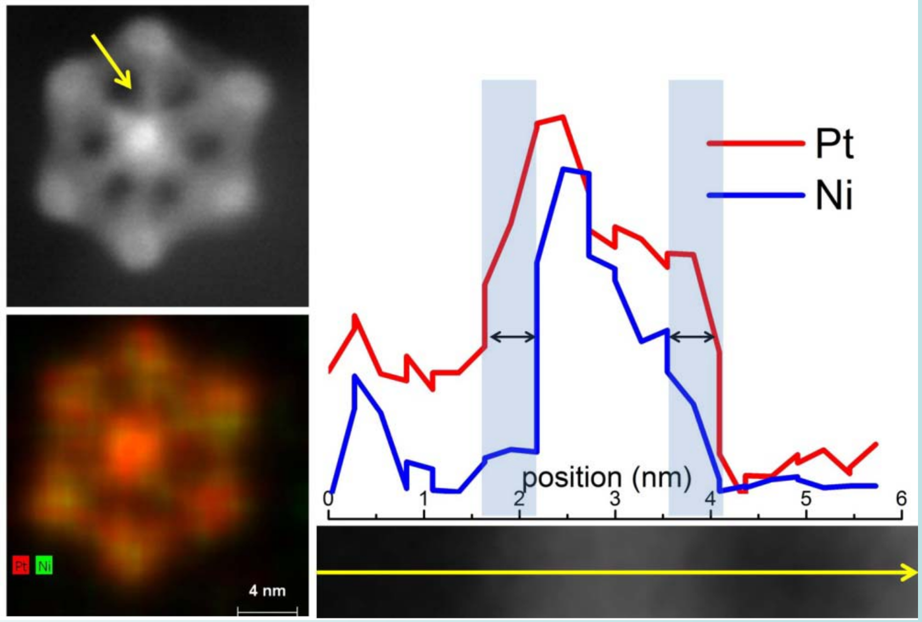
PtNi polyhedron: *elemental distribution*



PtNi polyhedron: ***as prepared***

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

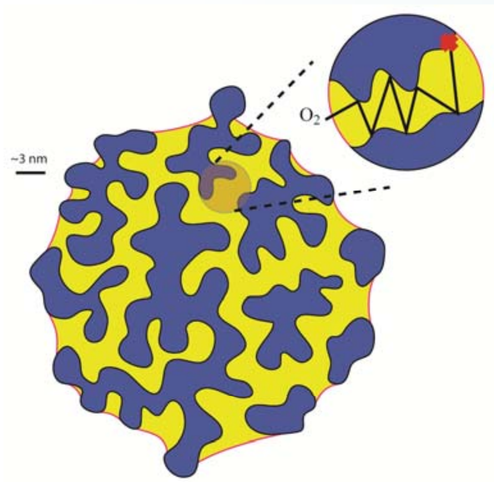




- **Narrow particle size distribution**
- **Hollow interior**
- **Formation of Pt-skin with the thickness of 2ML**
- **Surfaces with 3D accessibility for reactants**
- **Segregated compositional profile with overall Pt_3Ni composition**

Improving the ORR Rate by *Protic Ionic Liquids*

[MTBD][beti]

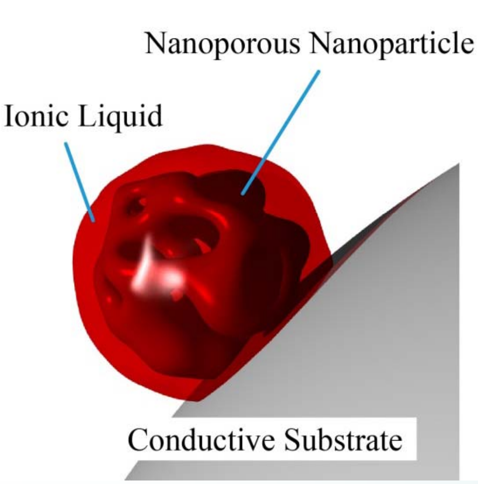


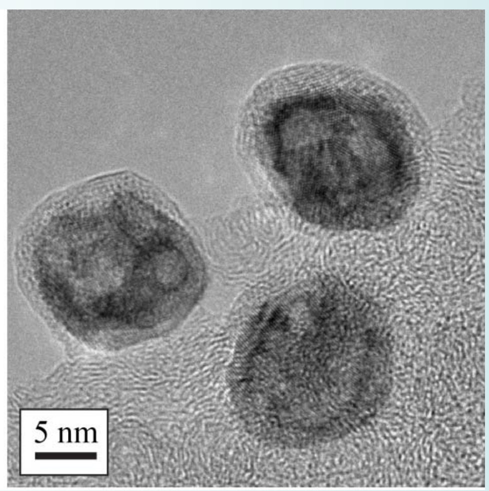
Chemically Tailored Interface

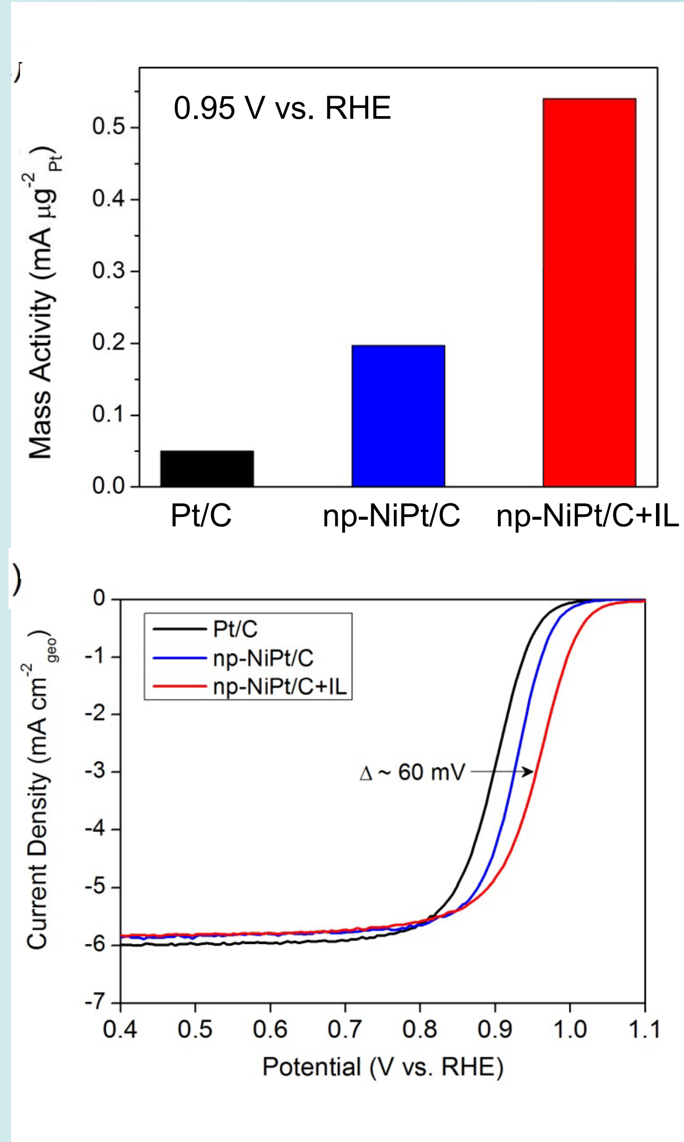
High O_2 solubility along with hydrophobicity yield improved ORR kinetics

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

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





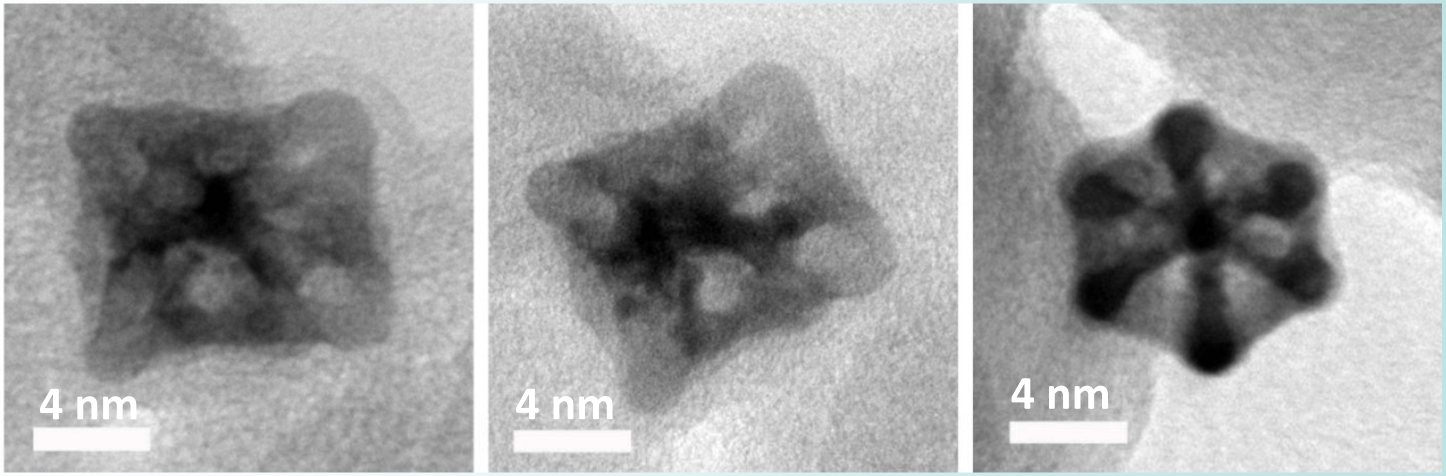


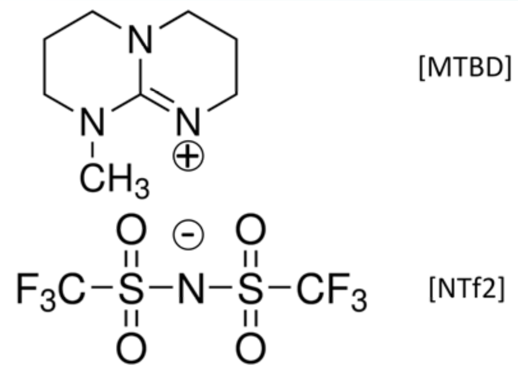
Argonne NATIONAL LABORATORY

Erlebacher and Snyder, *Advanced Functional Materials*, 23(2013)5494

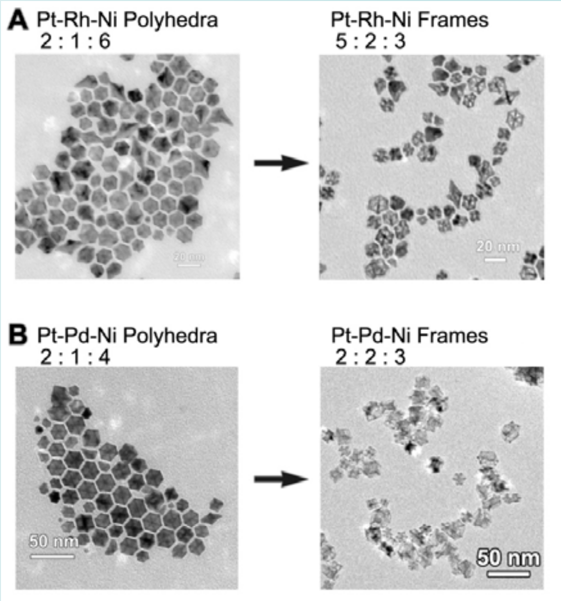
Tailoring Double Layer: *PtNi Nanoframes with Ionic Liquid*

Incorporation of Ionic Liquid Into the Nanoframes



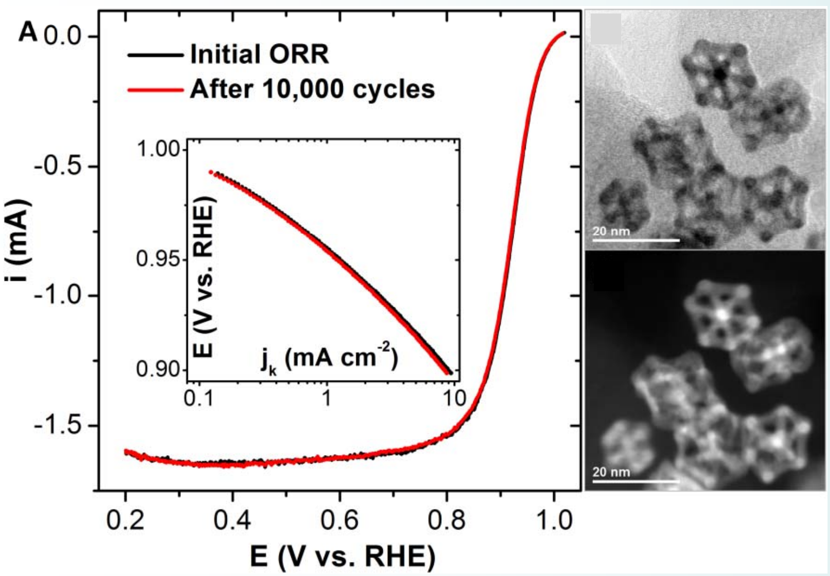


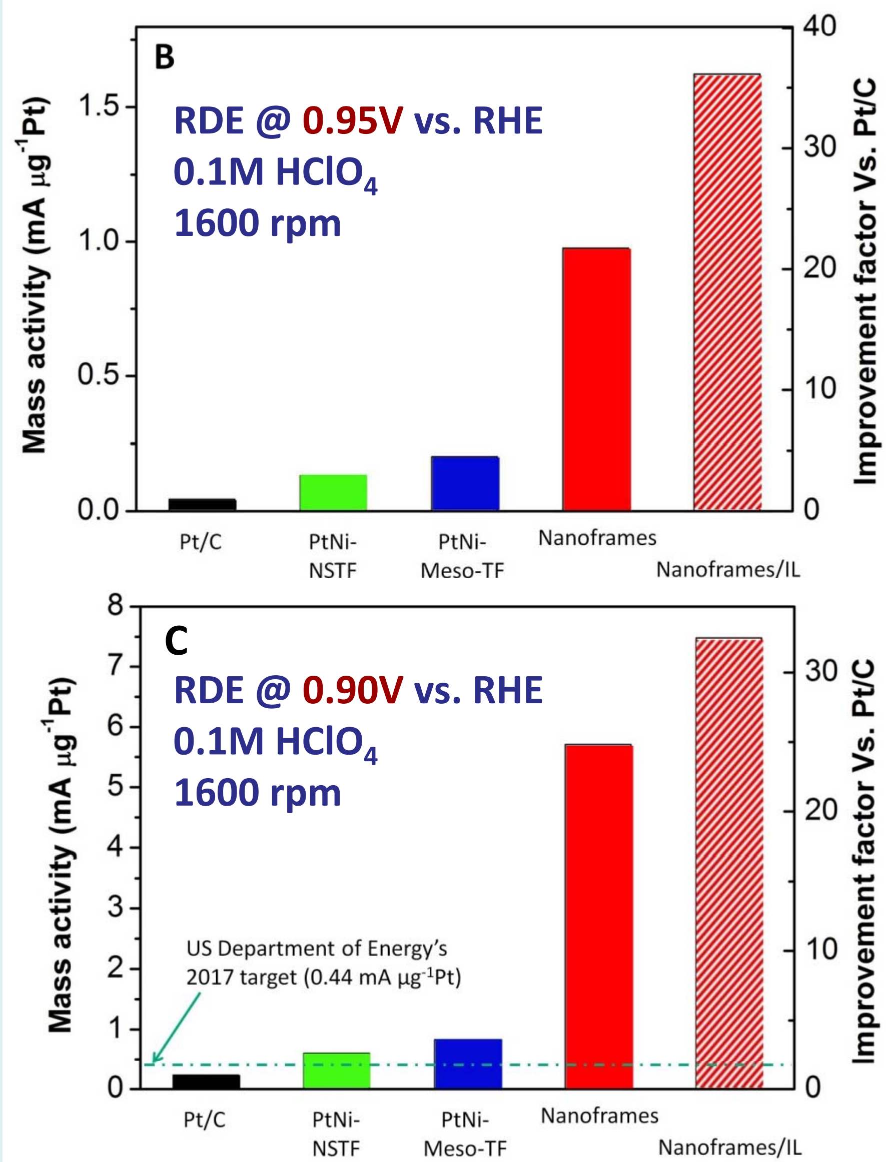
7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene [MTBD]



Science , 343 (2014) 1339

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

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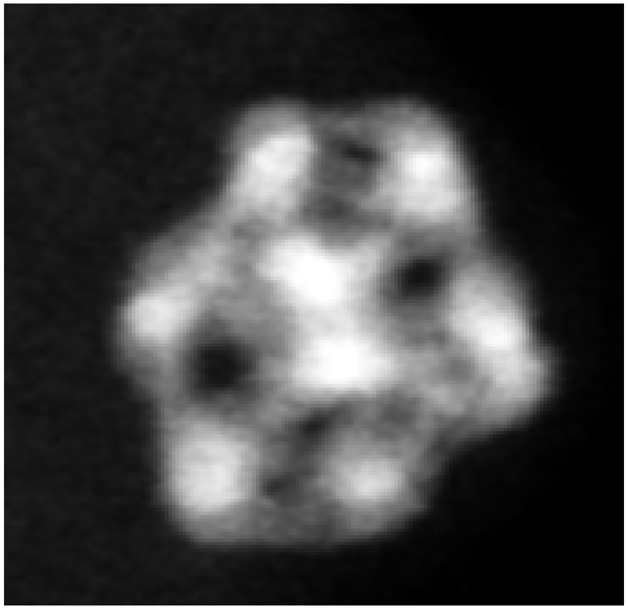
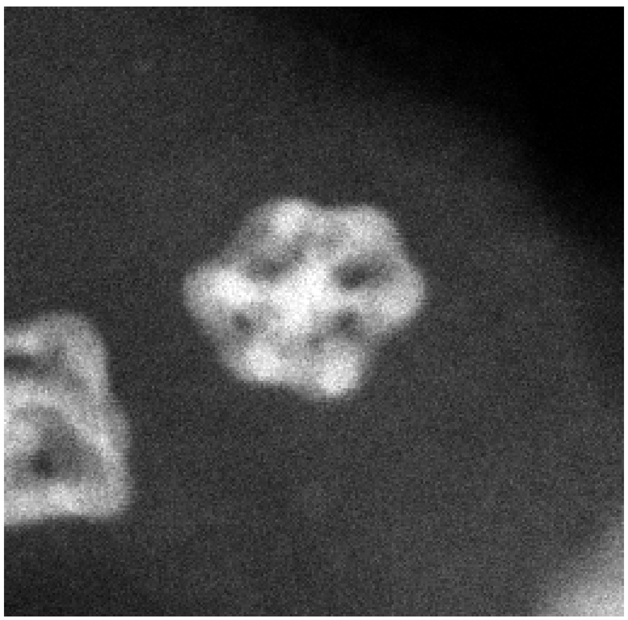
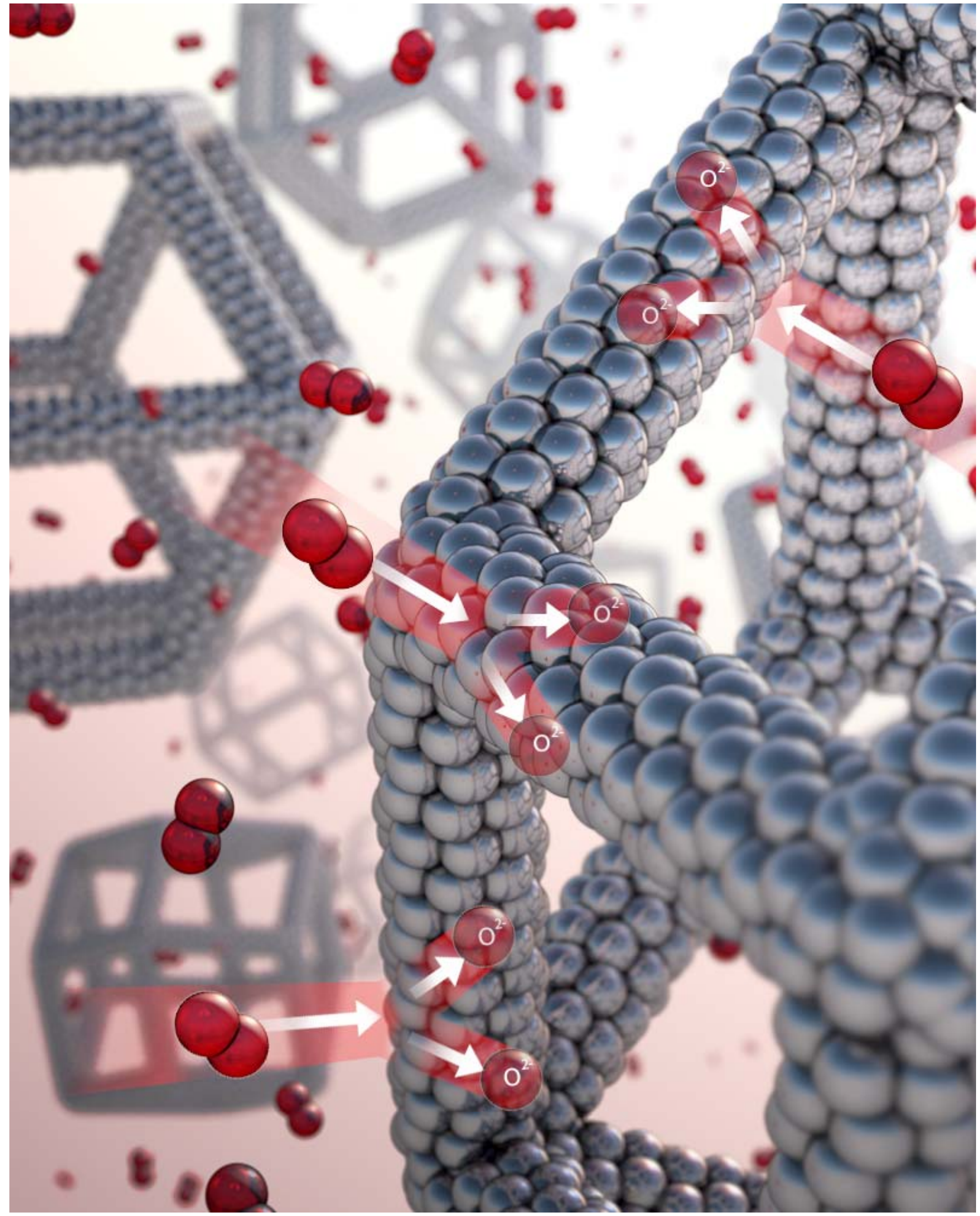
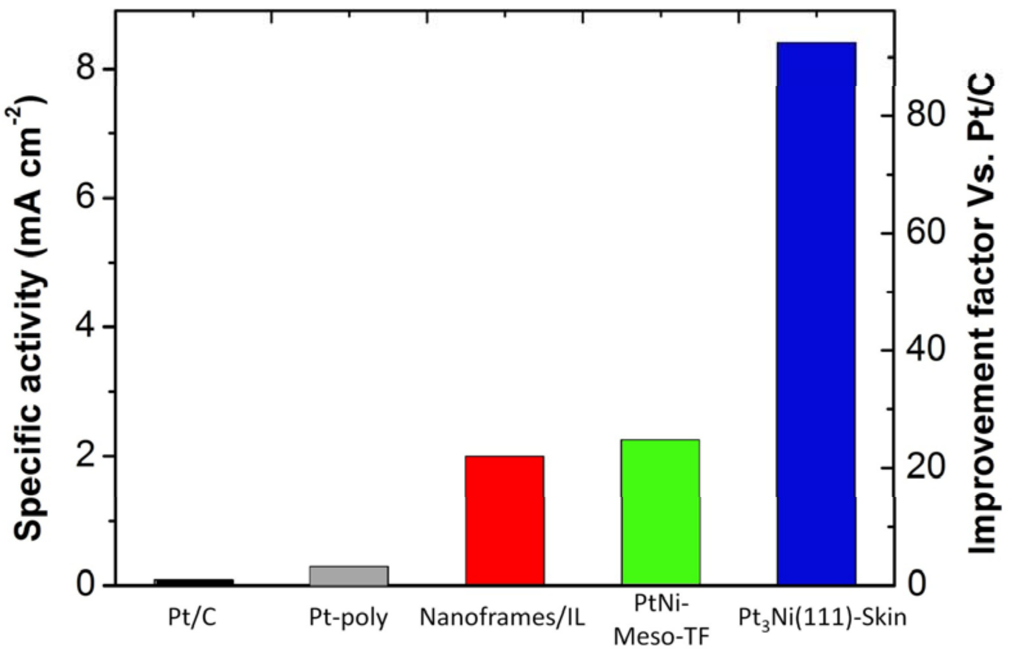
Multimetallic Nanoframes with 3D Electrocatalytic Surfaces





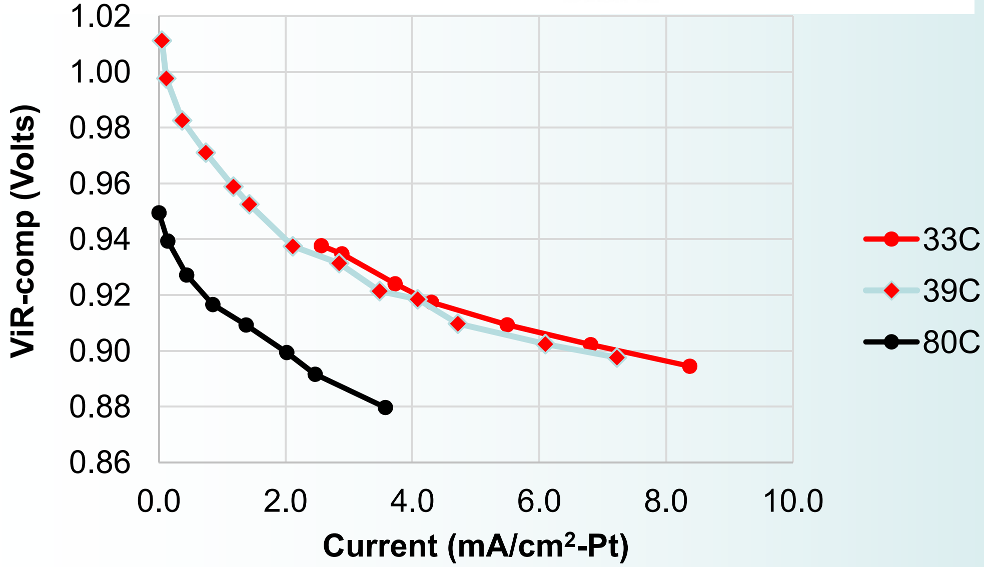


Specific Activities of Pt-Skin like Surfaces: *PtNi*



RDE

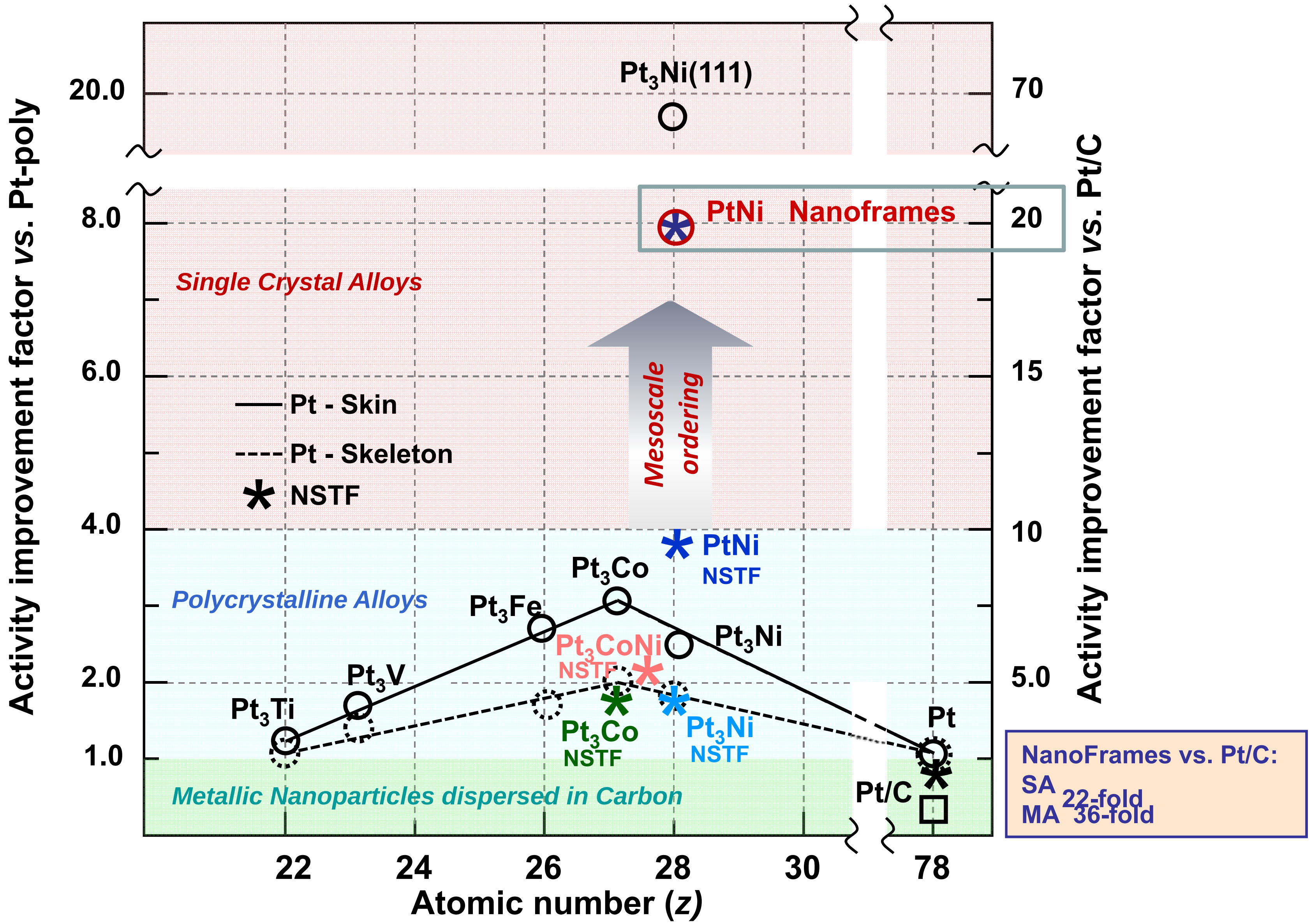
Bar chart showing the specific activities [normalized by ECSA(CO_{ad})] of Pt/C, Pt poly-crystal electrode (*3*), IL-encapsulated Pt_3Ni nanoframes/C, PtNi-Meso-TF (*3*), and $Pt_3Ni(111)$-Skin electrode (*3*), and corresponding improvement factors vs. Pt/C. The activities were measured at 0.95 V (vs. RHE), in 0.1 M $HClO_4$, on an RDE (1600 rpm).



MEA

Cathode: PtNi nanoframe, 0.05 mg-Pt/cm^2
Cathode ECSA: 28.3 cm^2 H_{upd}
Anode: 0.2 mg-Pt/cm^2 TKK 46 wt% Pt/HSC
Nafion XL membrane
GDL: Sigracet 25 BC

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



Activity | Durability | PGM Loading/Cost

Specific Activity — Electrochemical Stability — Mass Activity

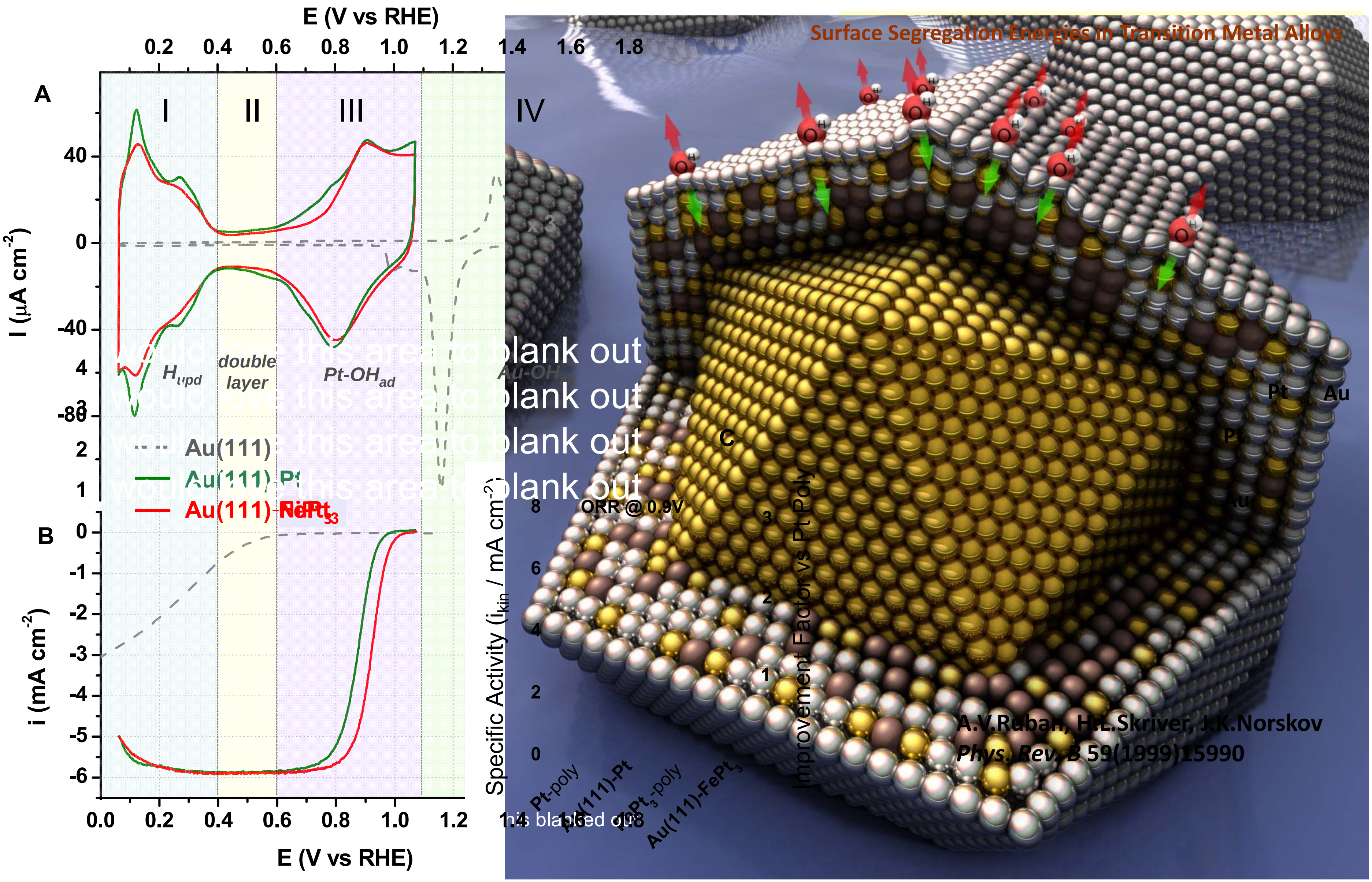
1° Surface Modifications

2° Tailored Electrolytes

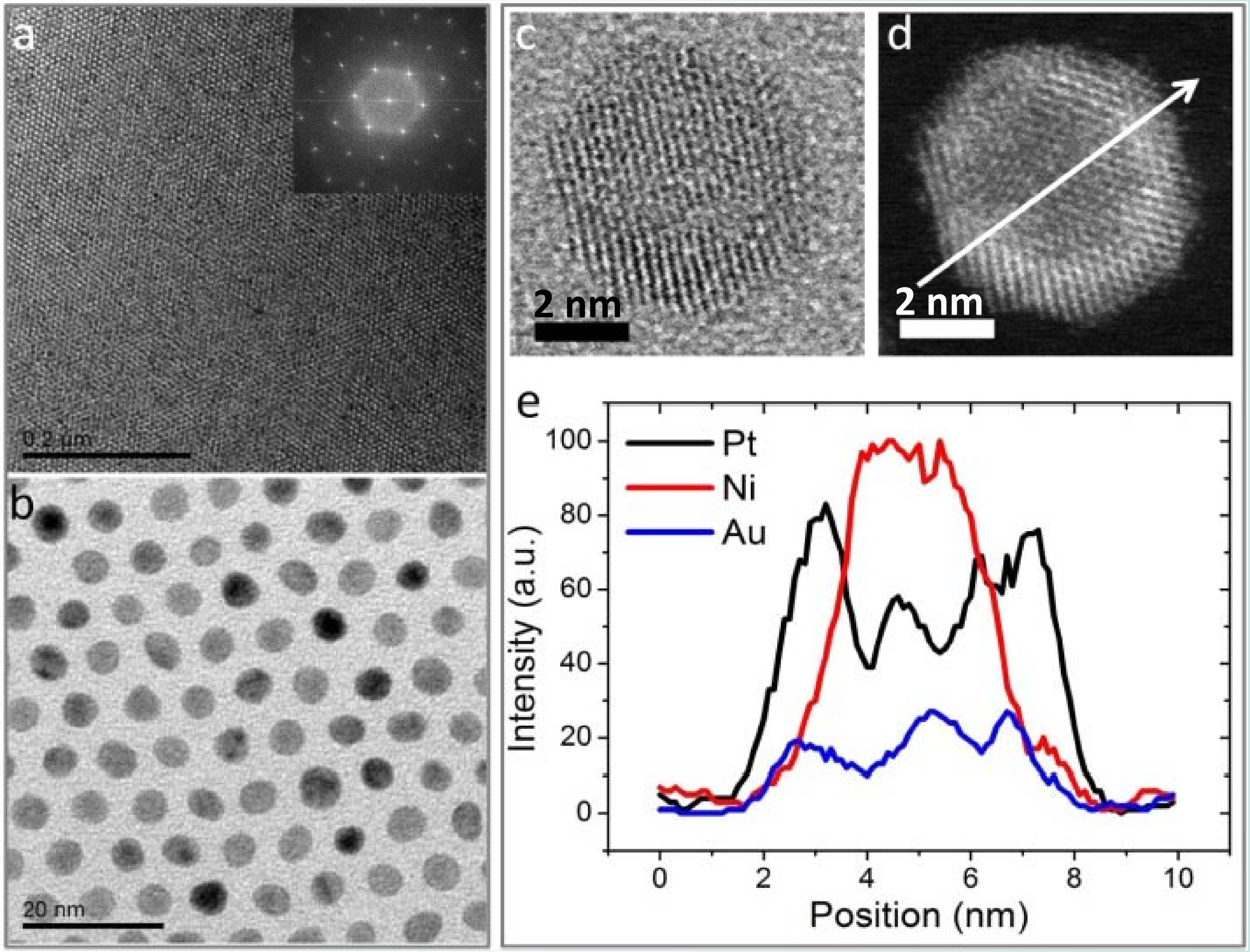
3° Structure-Function

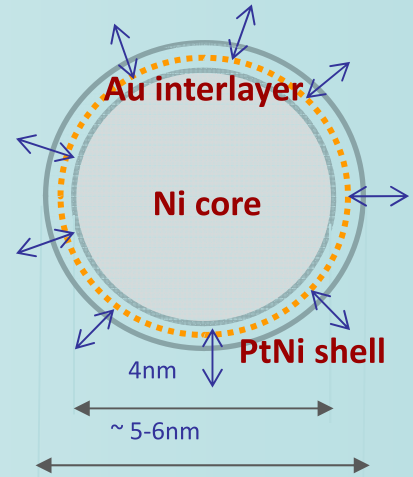
4° Composition-Function

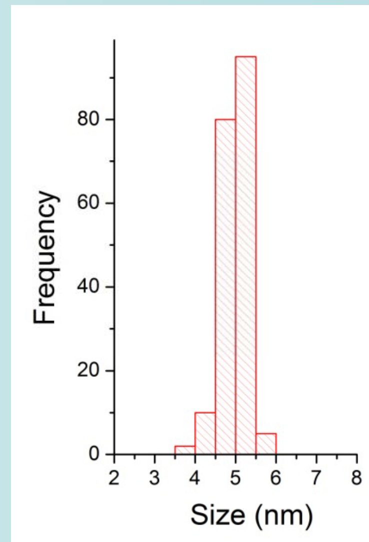
DURABILITY: *Mechanism of Improvement*



Synthesis of Core/Interlayer/Shell Electrocatalysts

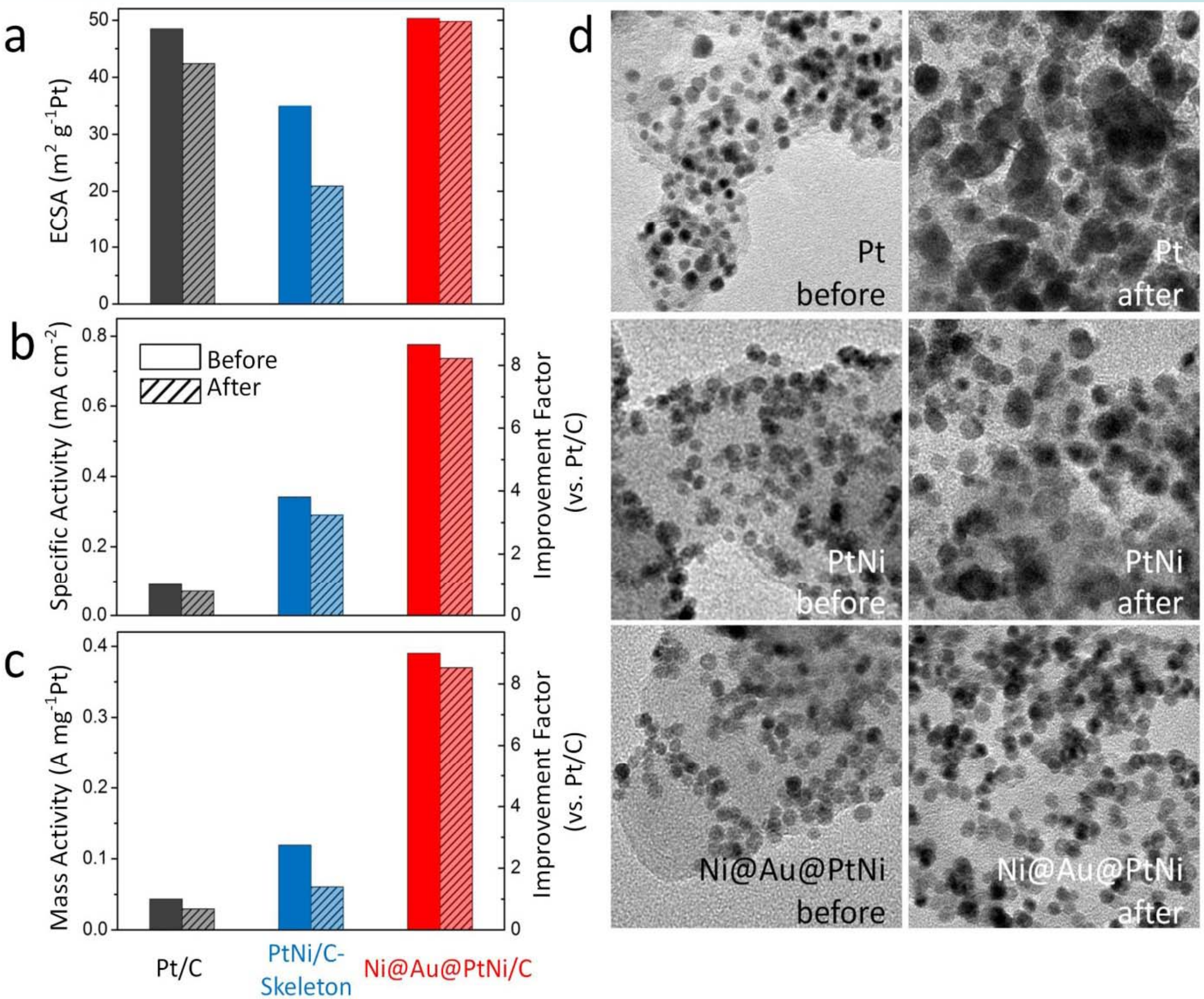




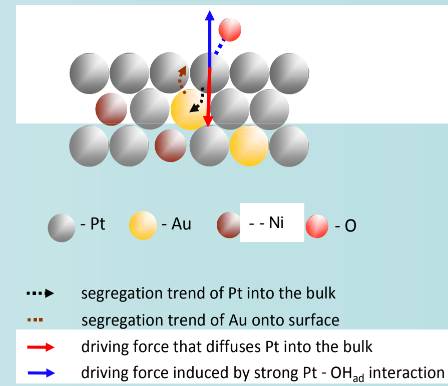


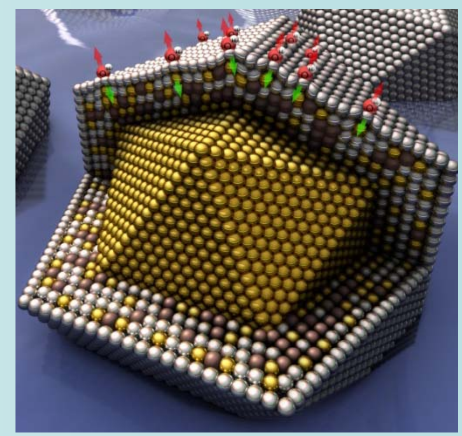
Monodisperse , Core/Interlayer/Shell NPs: Ni core / Au interlayer / PtNi shell

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



Stabilization mechanism





ELECTRIFIED SOLID-LIQUID INTERFACES

1 Reactants / Products

2 Electrode Material / Active Sites

3 Surface Structure — Surface Electronic Properties

4 (Sub)Surface Composition

5 NP Catalyst (Shape, Size, Support)

6 Electrolyte, Ions, pH, Impurities

7 Temperature [C]

8 Potential [V]

9 *Activity, Stability, Selectivity*