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Nanosegregated Cathode Catalysts with Ultra-Low Platinum Loading

Announcement No: DE-PS36-08GO98010

Topic: 1A

PIs: Vojislav R. Stamenkovic
Nenad M. Markovic

Materials Science Division

Argonne National Laboratory

Project ID#
FC008

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Overview

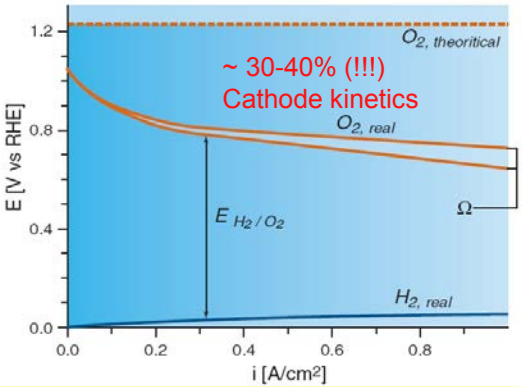
Timeline

- Project start: 9/2009
- Project end: 9/2014

Budget

- Total Project funding $ 5.1M
  - DOE share: 80 %
  - Contractor share: 20%
- Funding for FY13: $ 1.2M
- Planned FY14 DOE Funding: $763,856

Barriers



1) Durability of fuel cell stack

2) Cost (catalyst, membrane, gdl)

3) Performance (losses and activity)

Partners:

- **Oak Ridge National Laboratory** – Karren More
- **Jet Propulsion Laboratory** – C. Hays (FY10-12)
- **Brown University** – Shouheng Sun
- **University of Pittsburgh** – Goufeng Wang
- **3M Company** – Radoslav Atanasoski

Project Lead:

- **Argonne National Laboratory**

Relevance

Objectives **The main focus of ongoing DOE Hydrogen & Fuel Cell Program is development of highly-efficient and durable multimetallic PtMN (M, N = Co, Ni, Fe, V, T) *nanosegregated catalysts* for the oxygen reduction reaction *with ultra low-Pt content***

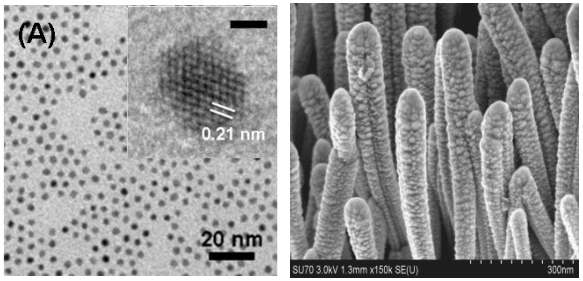
DOE Technical Targets

- 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

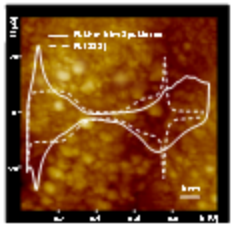
*based on Pt cost of $450/troy ounce

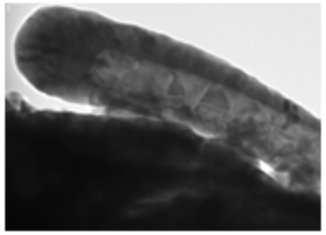
ANL Technical Targets

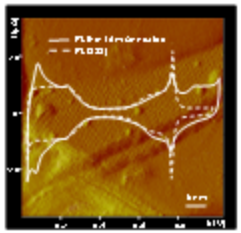
- Specific activity @ 0.9$V_{iR\text{-}free}$
  2015 DOE target x 3
- Mass activity @ 0.9$V_{iR\text{-}free}$
  2015 DOE target x 3
- Electrochemical area loss
  2015 DOE target
- PGM Total content
  < 0.1g/kW

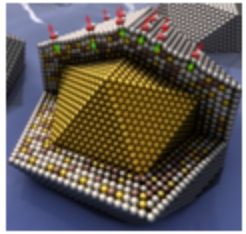


Approach









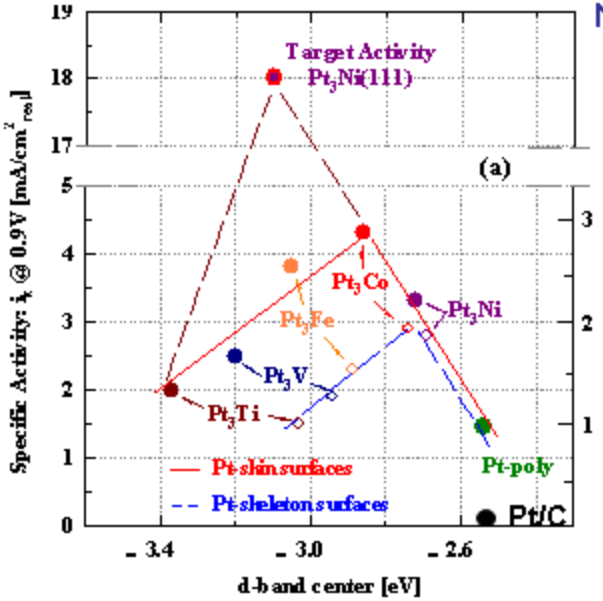
EXTENDED Multi-M SURFACES

THIN METAL FILMS / MODEL NANOPARTICLES

NANOPARTICLES

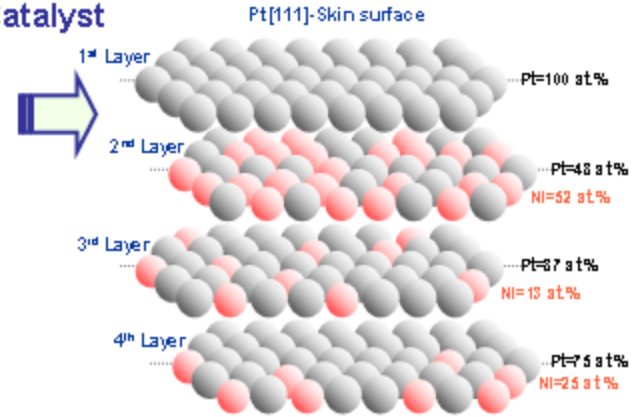
Materials-by-design approach - by ANL to design, characterize, understand, synthesize/fabricate, test and develop advanced nanosegregated multi-metallic nanoparticles and nanostructured thin metal films

Well-Defined Systems



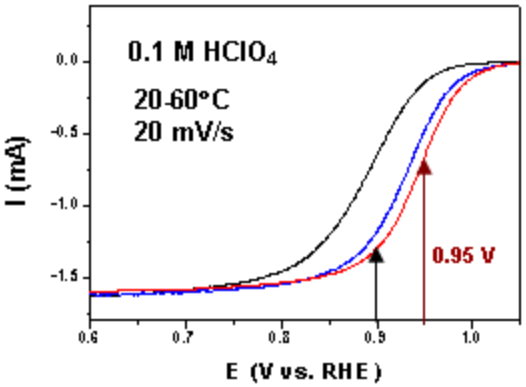
Advanced Nanoscale Catalyst

Nanosegregated Profile



Pt$_3$Ni(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

- Rational synthesis based on well-defined systems
- Addition of the elements that hinder Pt dissolution
- Activity boost by lower surface coverage of spectators
- Prevent loss of TM atoms without activity decrease

Approach / Milestone

(Go-No Go Decision Met)

Milestone 1. Fundamental understanding (FY09-13) (Accomplished)

1.1 Resolved electronic/atomic structure and segregation profile (100%)

1.2 Confirmed reaction mechanism of the ORR (100%)

1.3 Improved specific and mass activity (95%)

Milestone 2. Synthesis and characterization (FY10-14)

2.1 Physical methods: TM films (5-10 layers), nanoparticles (5-300 nm) (95%)

2.2 Established chemical methods: colloidal and impregnation synthesis (95%)

2.3 Characterization: Ex-situ (UHV, TEM) and in-situ (EXAFS, EC) (100%)

2.4 Theoretical modeling (DFT, MC) methods (95%)

Milestone 3. Fabrication and testing (FY11-14)

3.1 New PtM_1M_2 catalysts with higher activity and improved durability (95%)

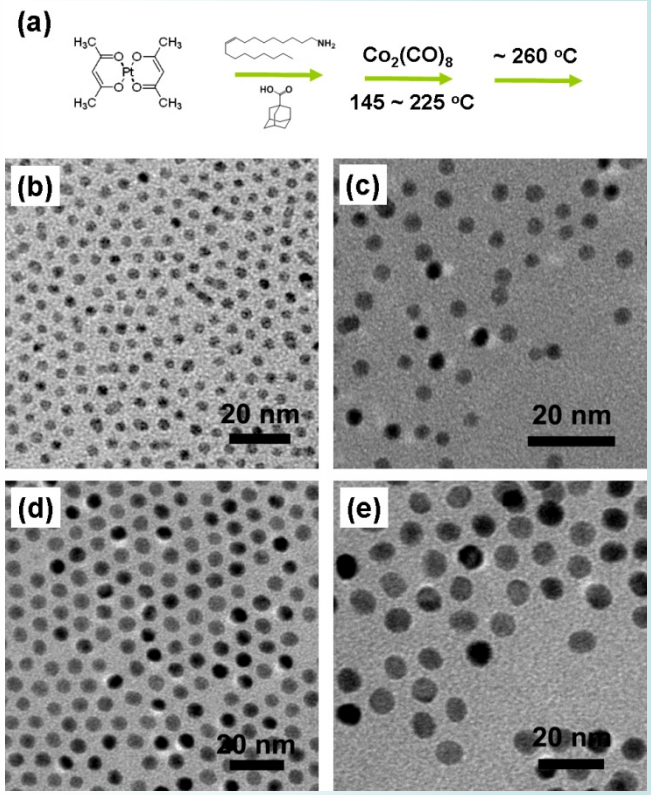
3.2 Carbon support vs. nanostructured thin film catalysts (95%)

3.3 MEA testing (50 cm^2) of the optimized catalysts (55%)

3.4 Scale up of the catalyst fabrication in lab environment (70%)

Technical Accomplishments FY09 -13: *Pt-alloy Nanocatalysts*

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

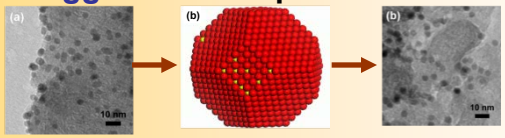
Mass Activity decreases with particle size

Optimal size particle size ~5nm

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

2º Temperature induced segregation in Pt-bimetallic NPs

Agglomeration prevented

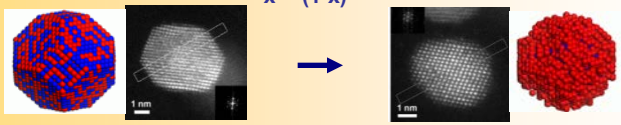


Optimized annealing temperature 400-500°C

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

3º Surface chemistry of homogeneous Pt-bimetallic NPs

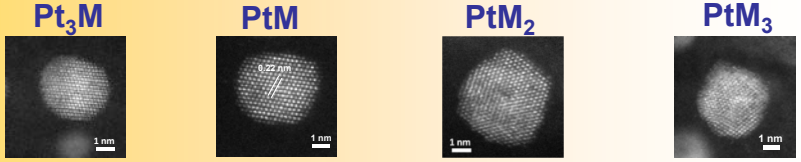
$Pt_xM_{(1-x)}$ NPs



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

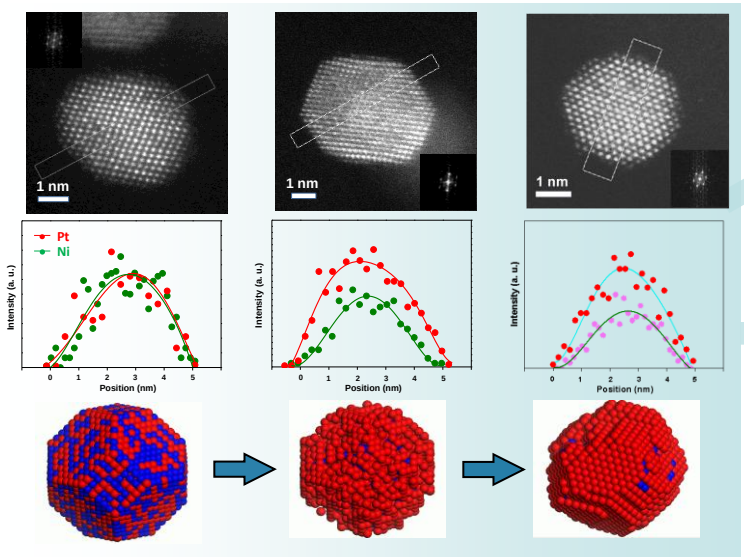
Adv. Funct. Mat., 21 (2011) 147

4º Composition effect in Pt-bimetallic NPs



Optimal composition of Pt-bimetallic NPs is PtM

Technical Accomplishments FY09-13: *Pt-alloy Nanocatalysts*

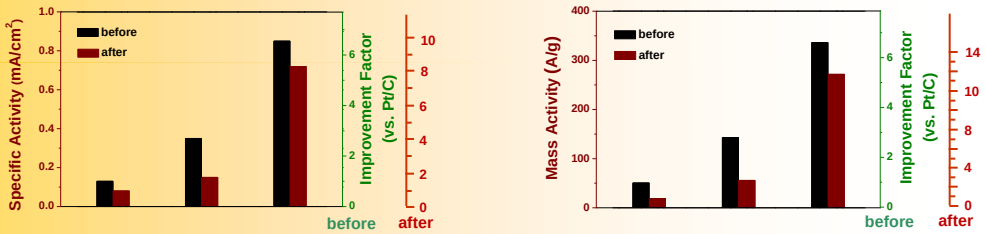


5º Pt-bimetallic catalysts with mutilayered Pt-skin surfaces

Synthesized PtNi NPs have homogeneous distribution of Pt, Ni

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

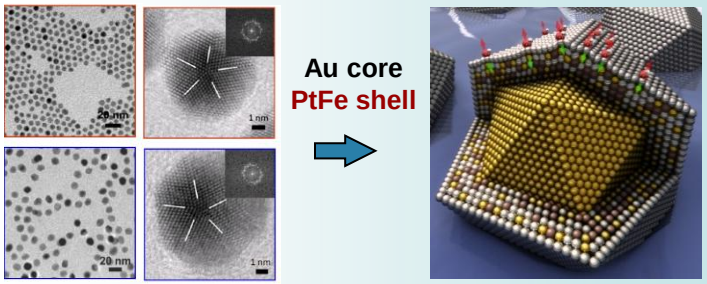
Multilayered Pt-skin surfaces confirmed for PtNi annealed NPs



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

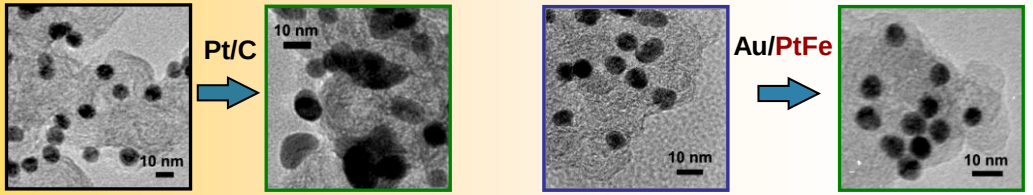
8-fold specific and 10-fold mass activity improvements over Pt/C

JACS, 133 (2011) 14396

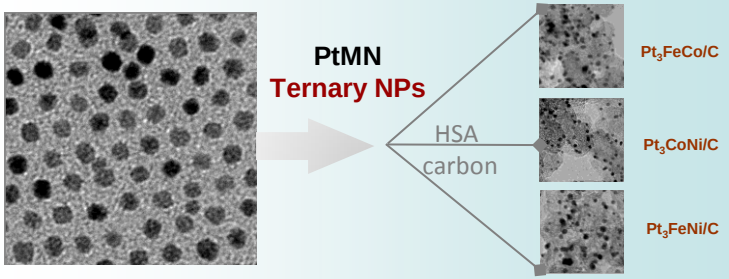


Au core
PtFe shell

6º Multimetallic NPs can further improve activity and durability



Nano Letters, 11 (2011) 919



PtMN
Ternary NPs

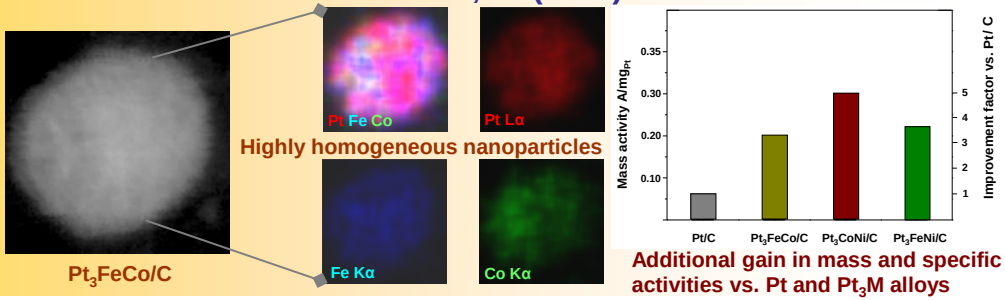
HSA carbon

Pt_3FeCo/C

Pt_3CoNi/C

Pt_3FeNi/C

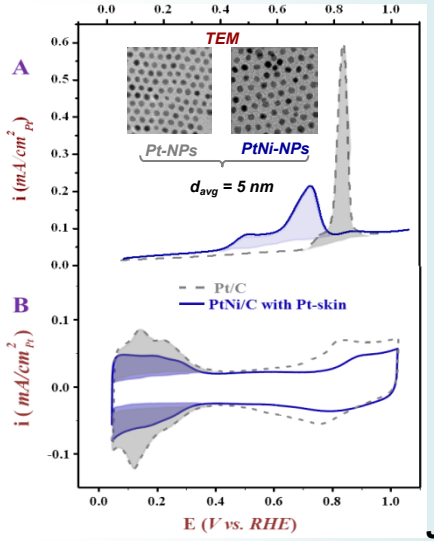
J. Phys. Chem. Letters, 3 (2012) 1668

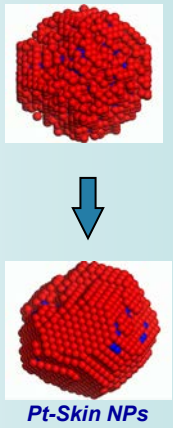


Pt_3FeCo/C

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

Technical Accomplishments FY09-13: *Pt-alloy Nanocatalysts*





JACS 133 (2011) 14396

7º Electrochemically active surface area of Pt-Skin catalysts

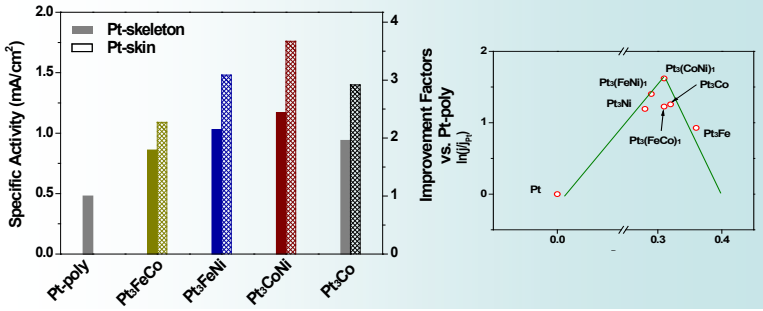
Catalysts with multilayered Pt-skin surfaces exhibit substantially lower coverage by H_{upd} vs. Pt/C
(up to 40% lower H_{upd} region is obtained on Pt-Skin catalyst)

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

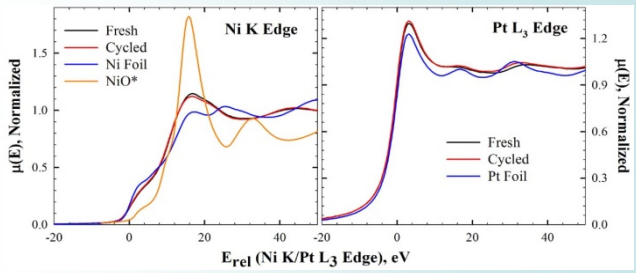


8º Multimetallic Pt_3NM alloys can further improve activity

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

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



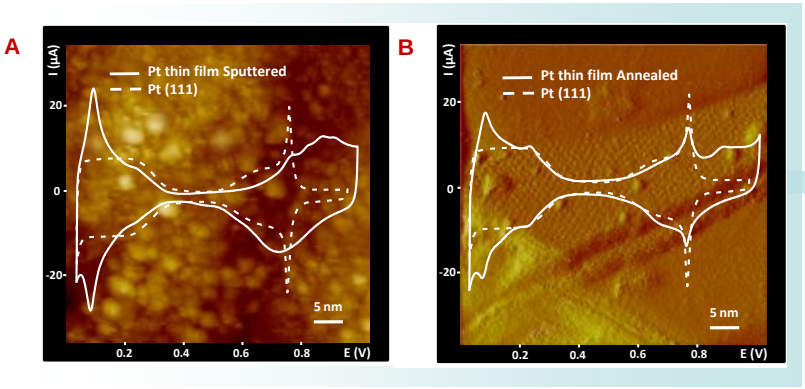
9º MEA: PtNi-MLSkin/NPs 20,000 potential cycles, 0.6 – 0.95 V

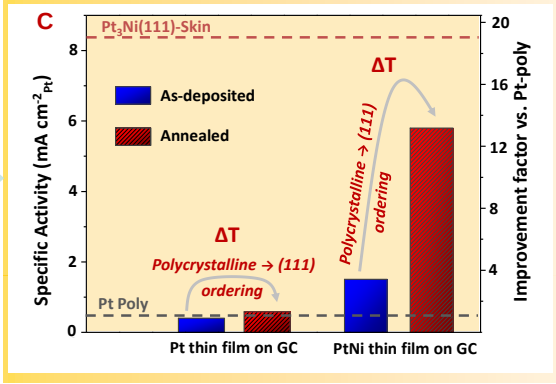
No change in Ni and Pt edges after 20K cycles confirms high stability pf multilayered Pt-Skin under operating conditions

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

Unpublished

Technical Accomplishments FY09-13: *Pt-alloy Nanocatalysts*



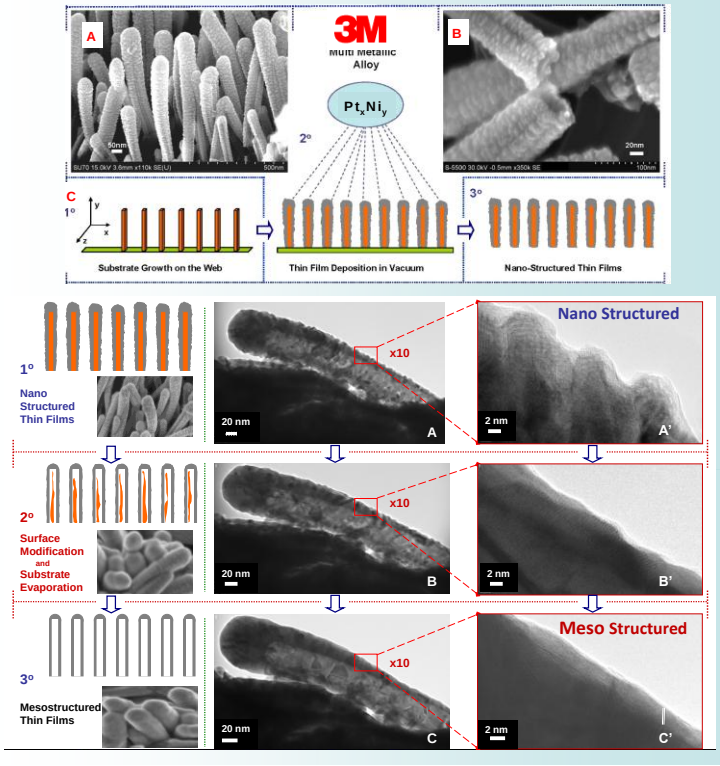


Scientific Achievement

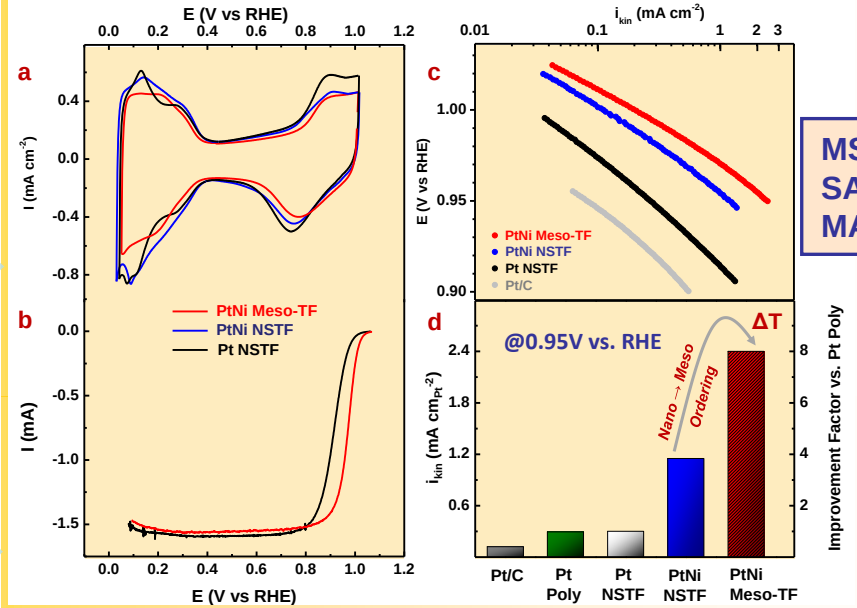
Control of surface structure and morphology of multimetallic thin films without use of templates for epitaxial growth

Significance and Impact

Enables electrocatalytic properties of Pt-alloy single crystals in thin film materials



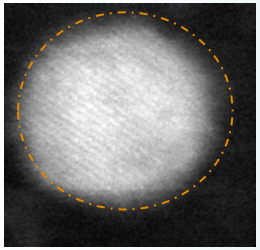
10° Mesostructured Thin Films with Tunable Morphology

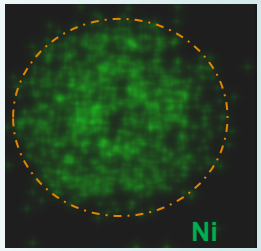


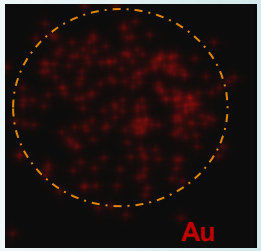
MSTF vs. Pt/C:
SA 20-fold
MA 6-fold

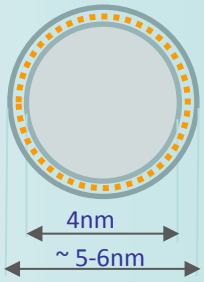
Nature Materials, 11 (2012) 1051

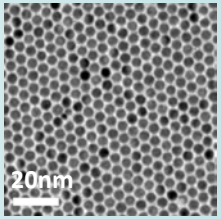
Technical Accomplishments FY09-13: *Pt-alloy Nanocatalysts*



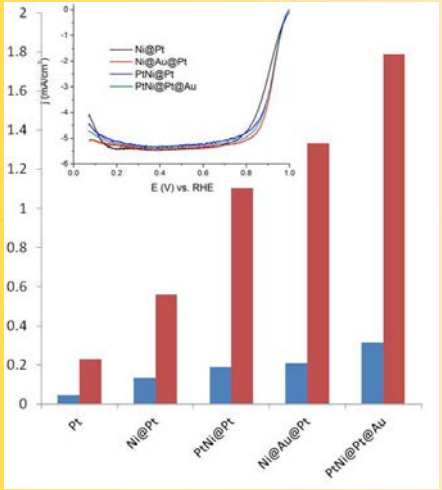


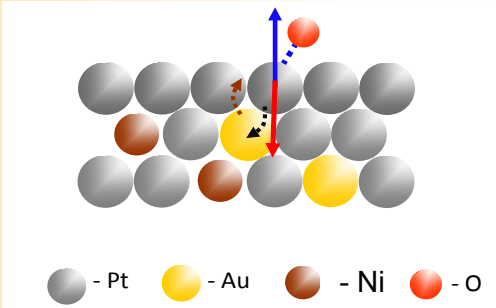






11º Core-Shell particles with Au interlayer





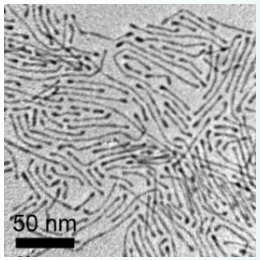
segregation trend of Pt into the bulk

segregation trend of Au onto surface

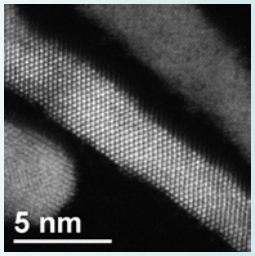
driving force that diffuses Pt into the bulk

driving force induced by strong Pt - OH_{ad} interaction

Unpublished

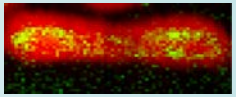


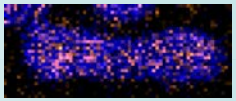
$Co_{32}Pt_{68}$ → $Co_{12}Pt_{88}$

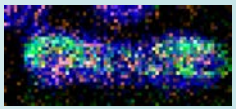


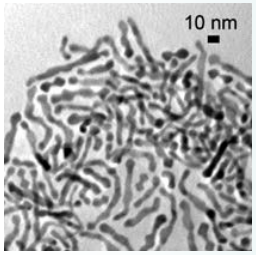
highly crystalline

segregation profiles

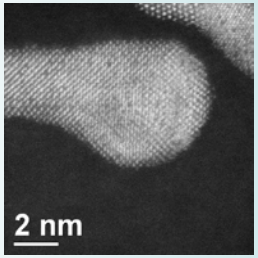




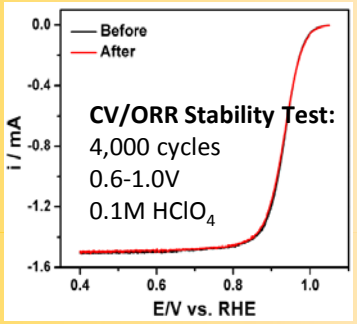


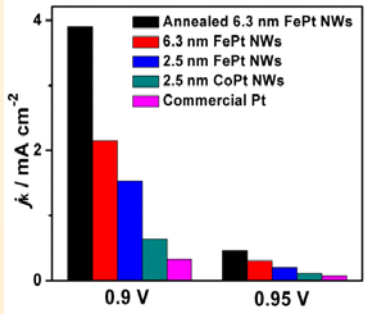


width 5.5 nm



12º Highly active and durable multimetallic NWs





Pt Alloy NWs are active and durable catalyst with no change in activity after 4,000 cycles

Specific activity depends on the composition and width of NWs

Annealing of NWs induces formation of nanosegregated profile with Pt-Skin type of surface

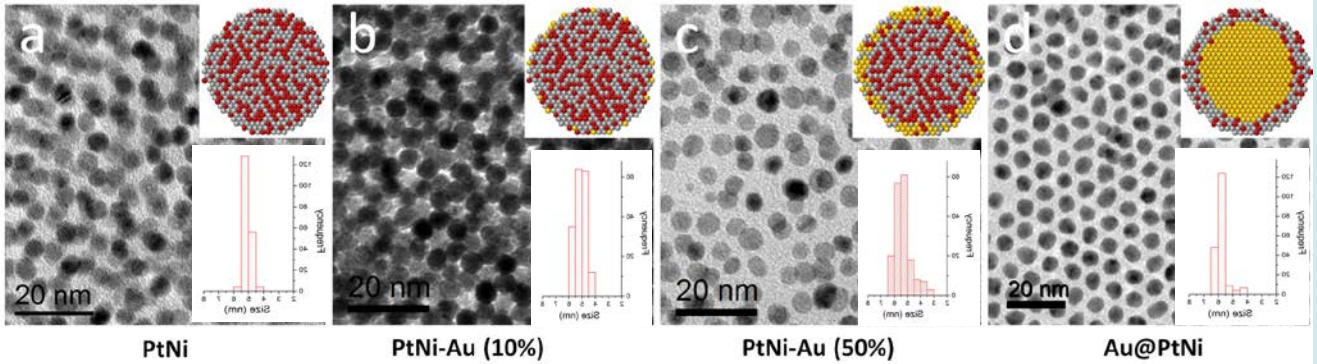
Pt-Skin confirmed by suppressed H_{upd}, Pt-OH shift, CO_{ad}/Hupd ratio, and high ORR activity

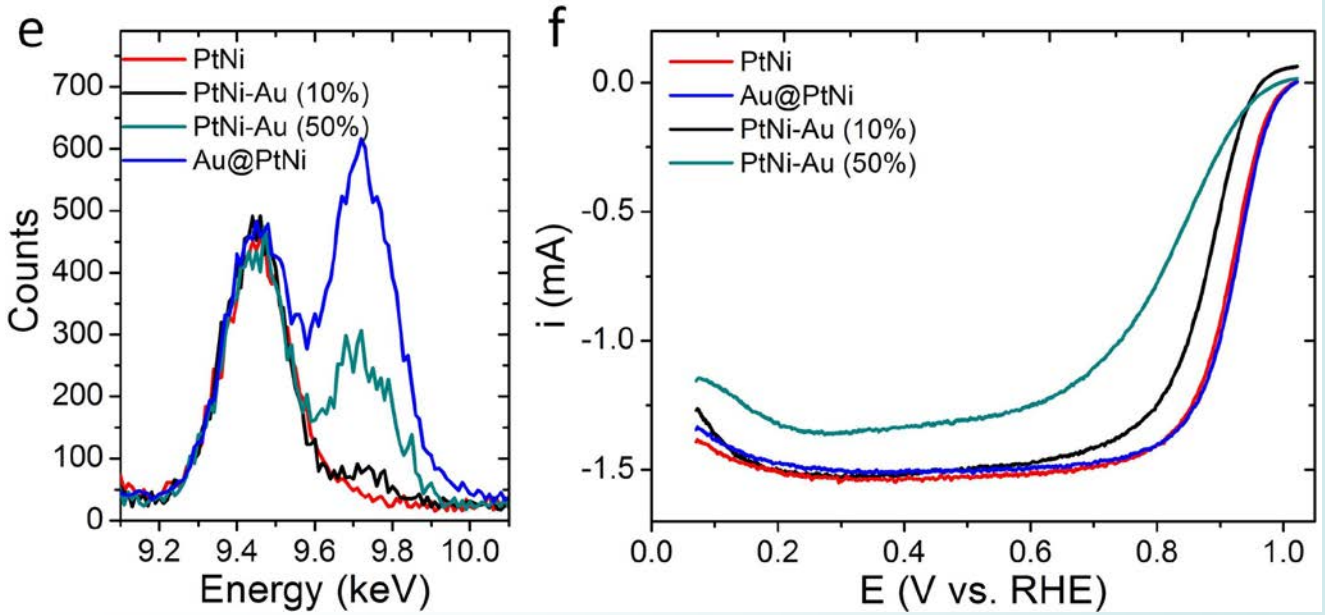
***Angew. Chem. Int.Ed.*, 52 (2013) 3465**

Accomplishments and Progress: *Core/Shell NPs with Au interlayer*

Synthesis, Structural and Electrochemical evaluation of core shell NPs

Influence of surface Au on the ORR catalytic performance

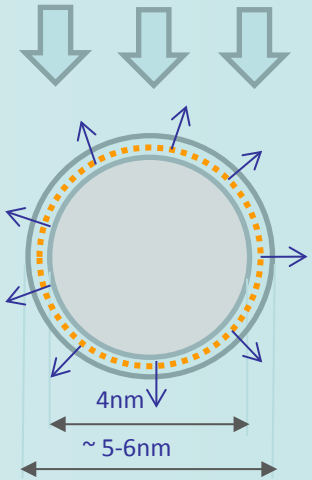




Surface Au decreases total number Pt active sites for adsorption of O_2

Au core / PtNi shell NPs have the same catalytic activity as PtNi NPs

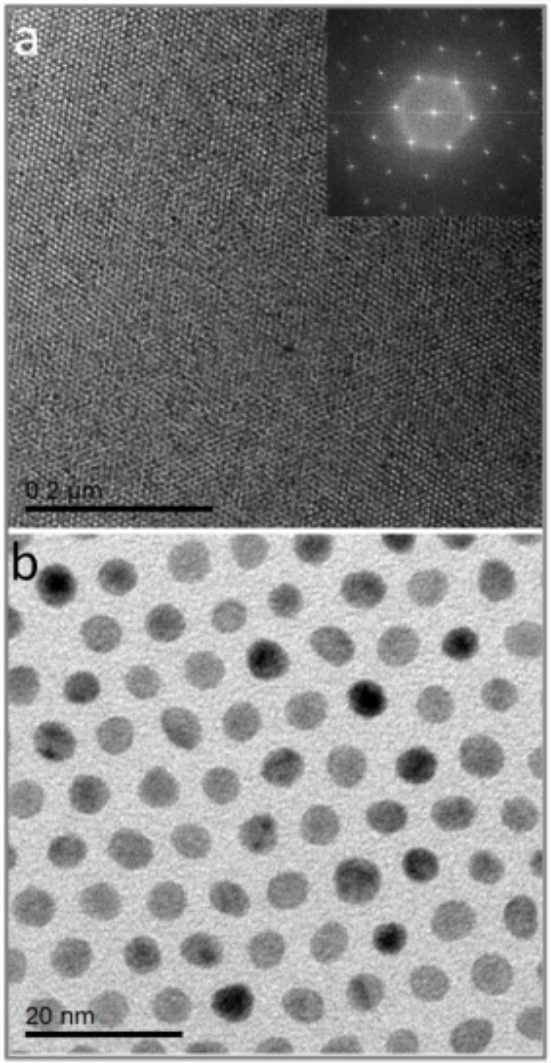
Subsurface Au does not alter catalytic properties of NPs

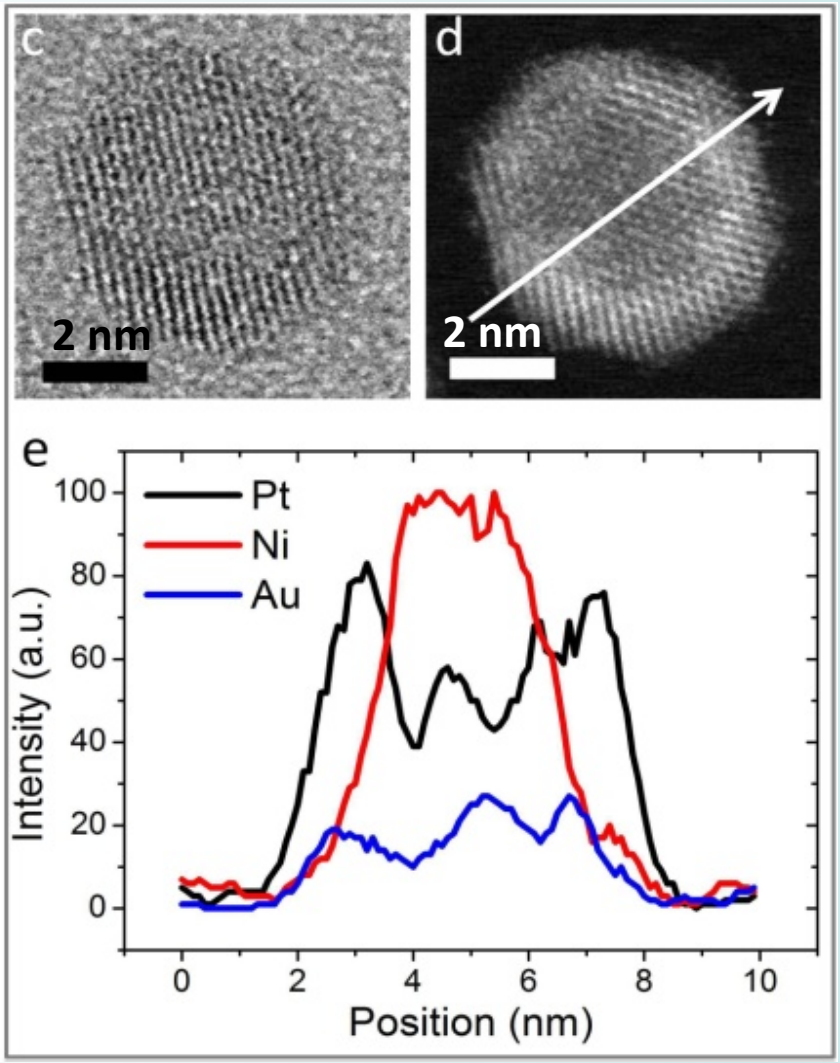


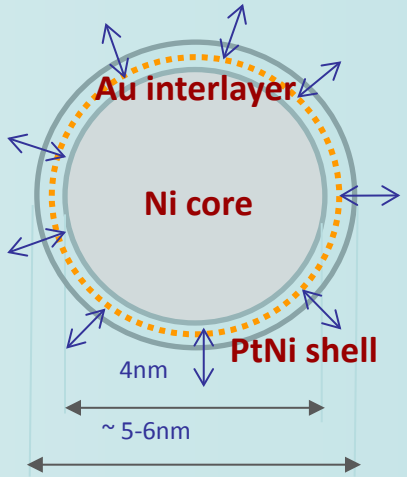
Ni core / Au interlayer / PtNi shell

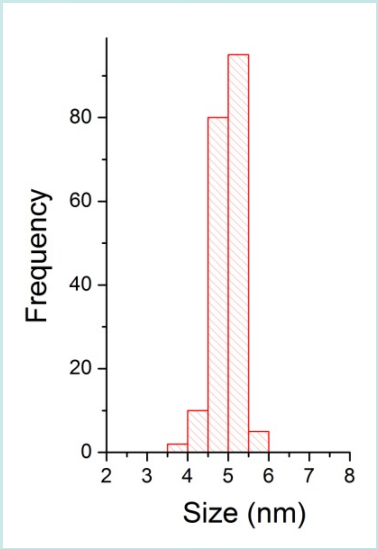
Accomplishments and Progress: *Core/Shell NPs with Au interlayer*

Synthesis, Structural and Electrochemical evaluation of core shell NPs





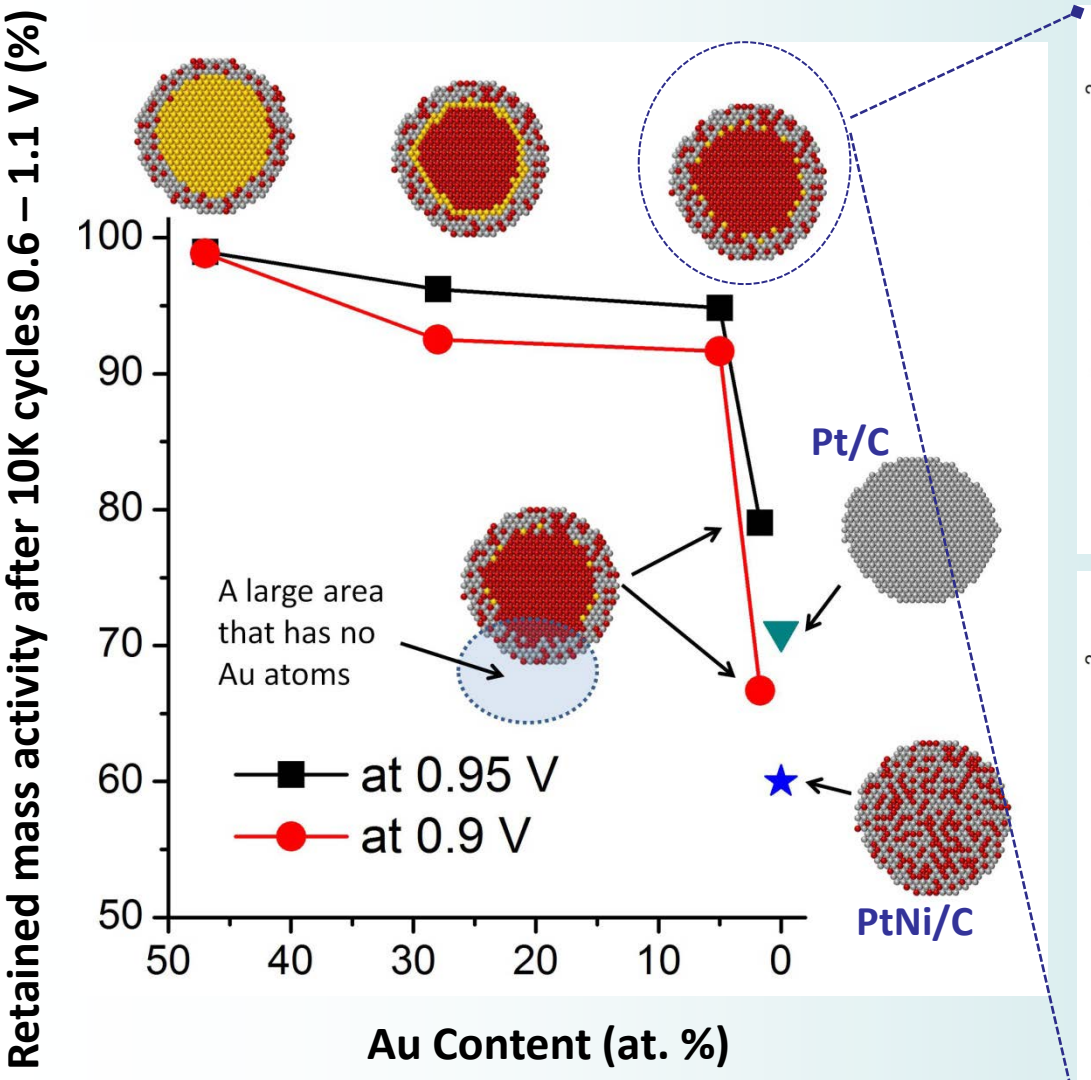


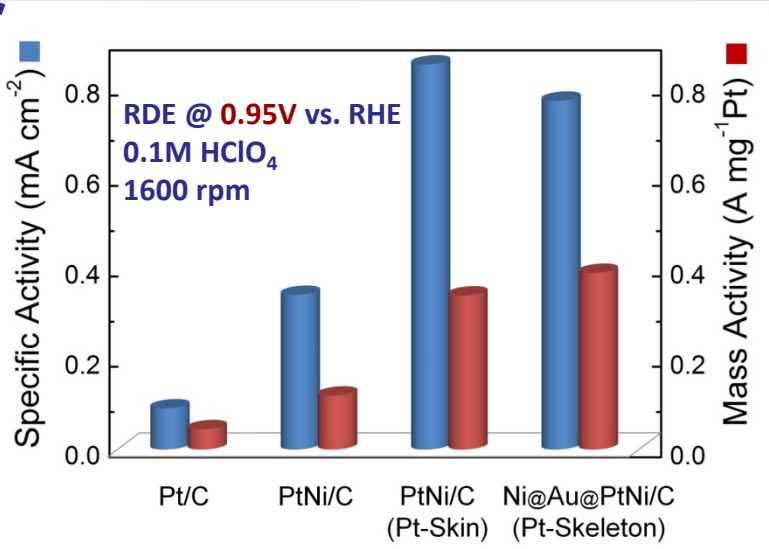


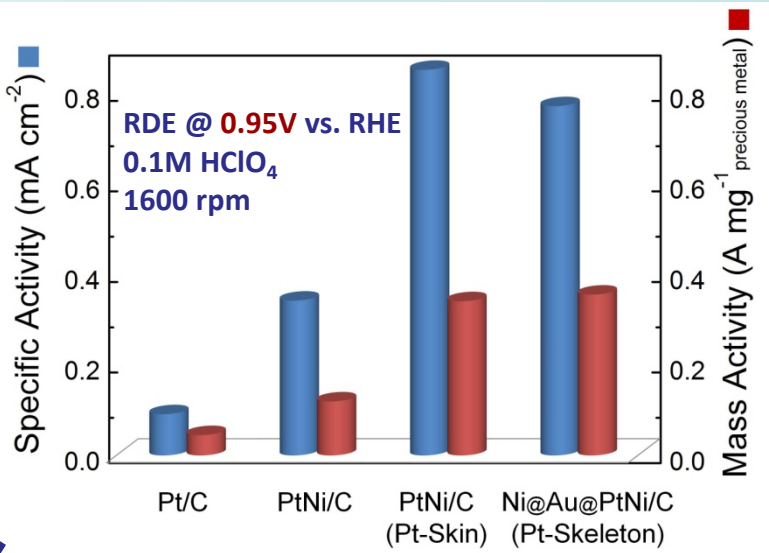
Monodisperse , Core/Interlayer/Shell NPs: Ni core / Au interlayer / PtNi shell

Accomplishments and Progress: *Core/Shell NPs with Au interlayer*

Synthesis, Structural and Electrochemical evaluation of core shell NPs

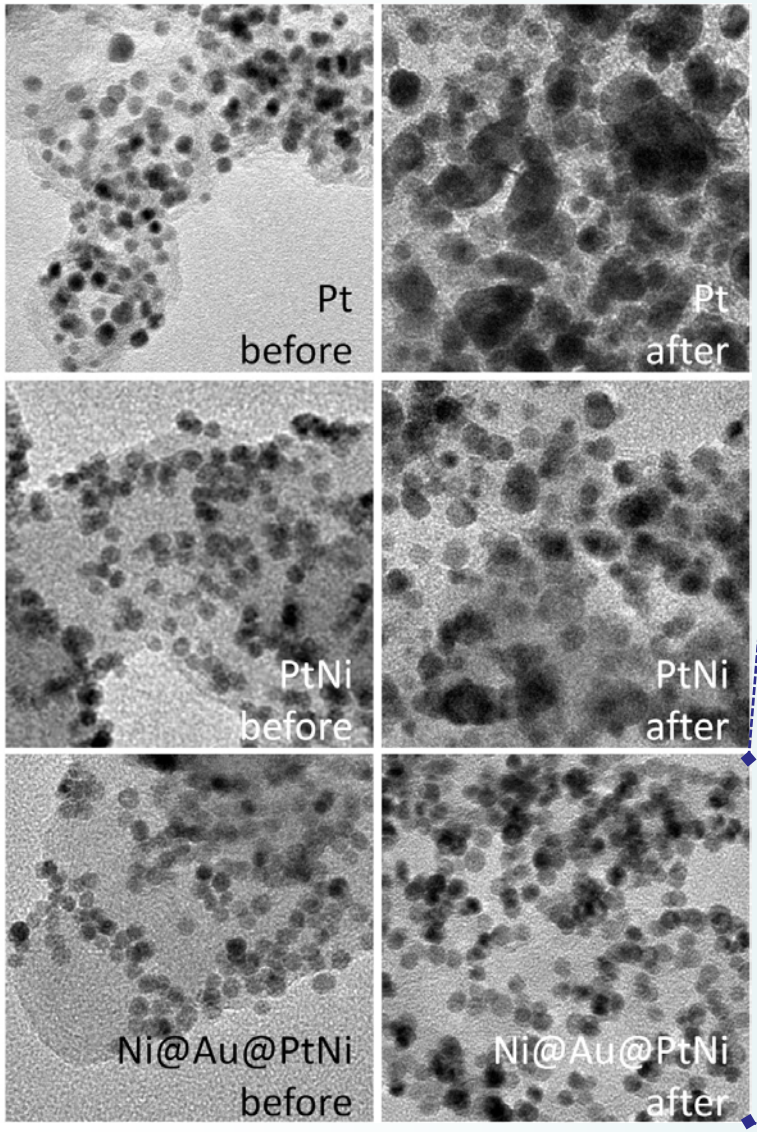


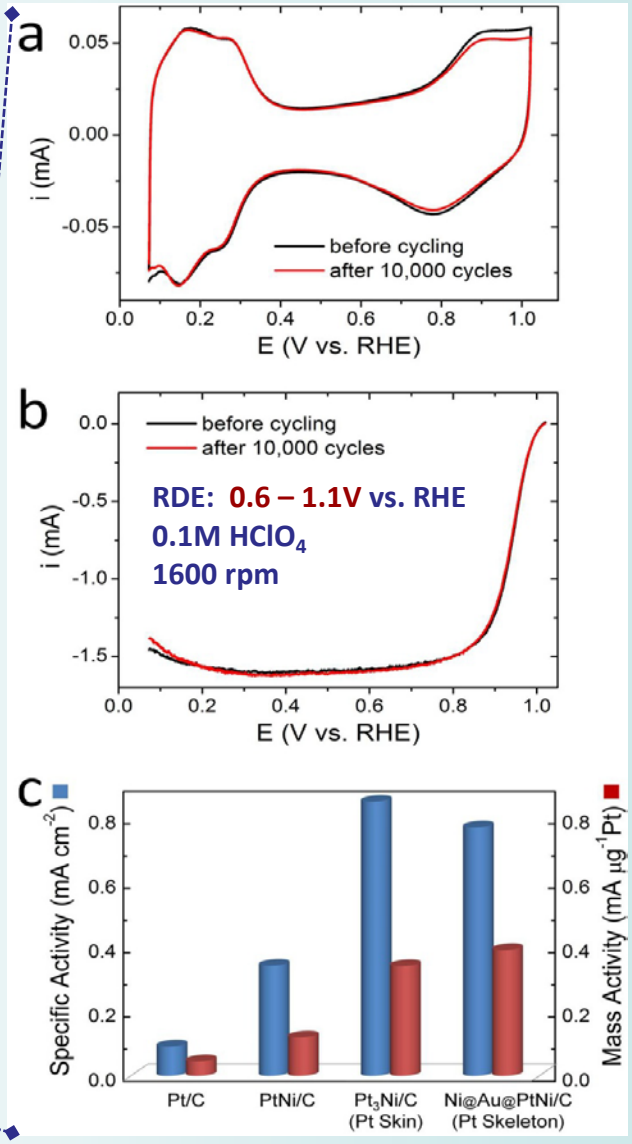




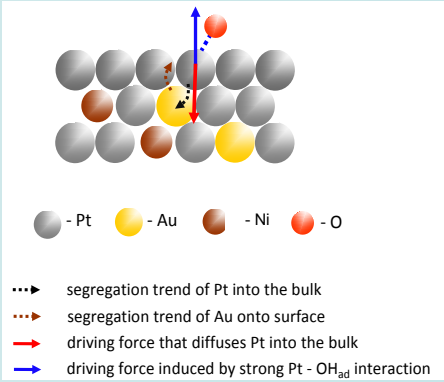
Accomplishments and Progress: *Core/Shell NPs with Au interlayer*

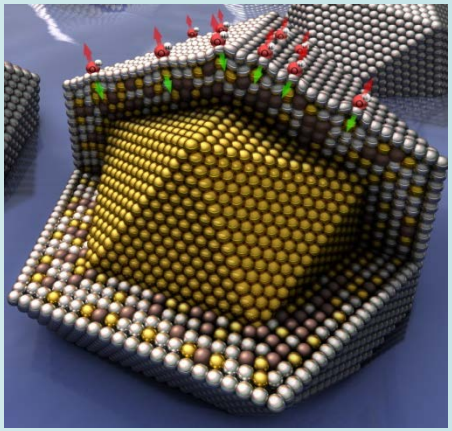
Synthesis, Structural and Electrochemical evaluation of core shell NPs





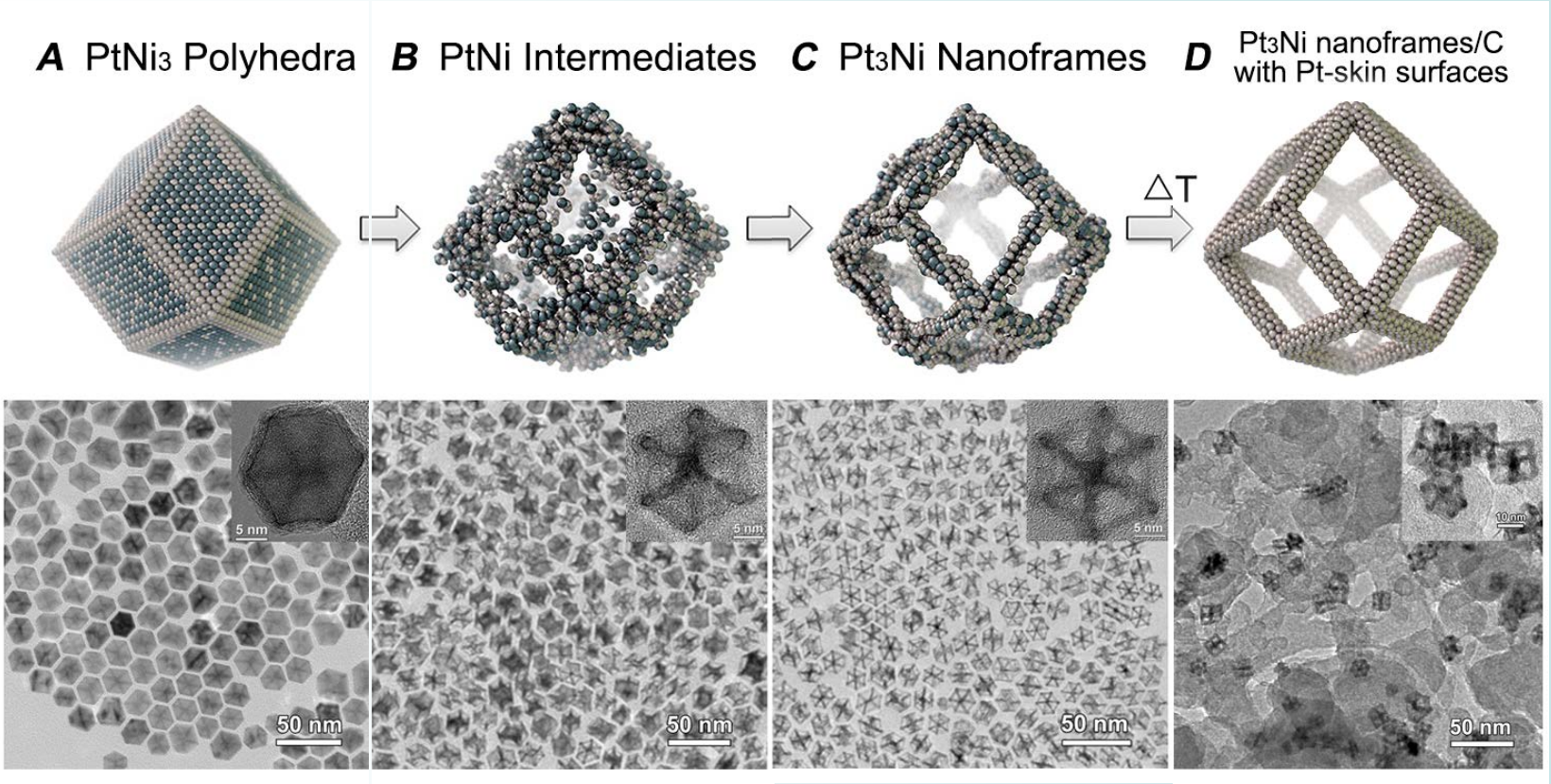
Stabilization mechanism





Accomplishments and Progress: *PtNi Nanoframes*

Synthesis, Structural and Electrochemical evaluation of Nanoframes



- 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

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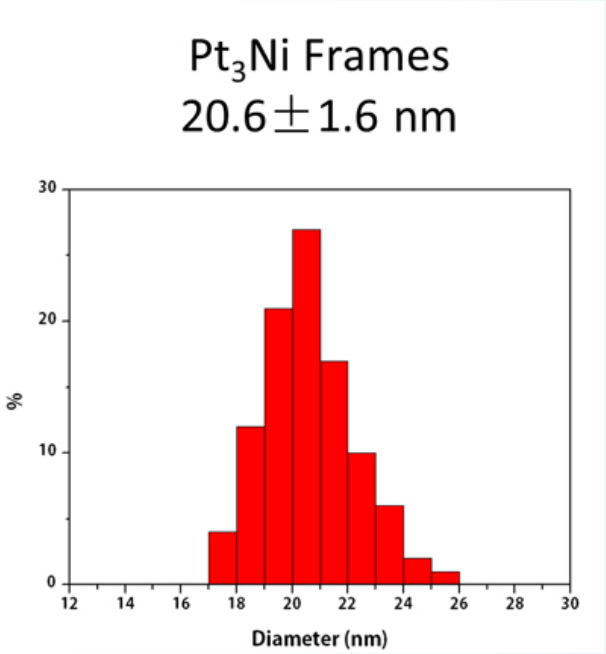
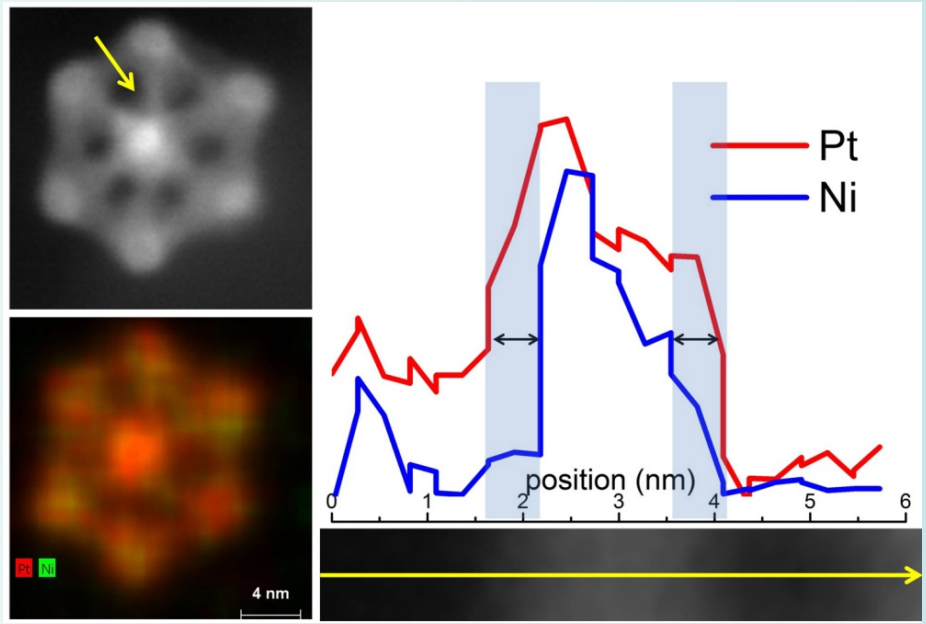
Accomplishments and Progress: *PtNi Nanoframes*

Synthesis, Structural and Electrochemical evaluation of Nanoframes

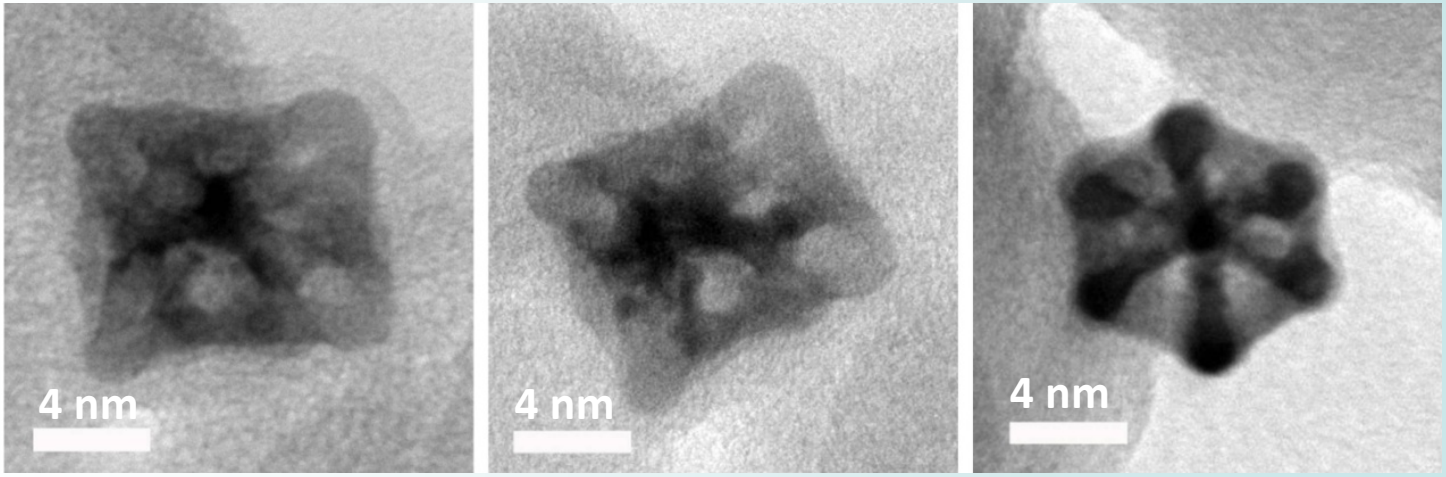


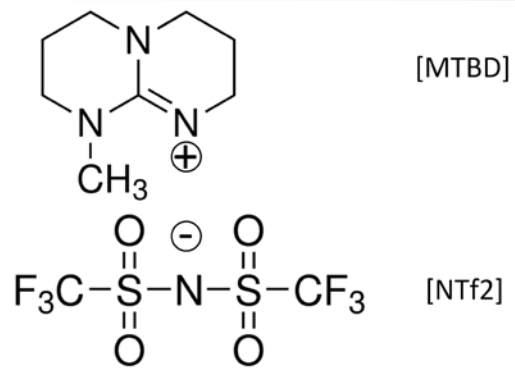


- Narrow particle size distribution
- Hollow interior
- Formation of Pt-skin with the thickness of 2ML
- Surfaces with 3D accessibility for reactants
- Segregated compositional profile with overall Pt_3Ni composition

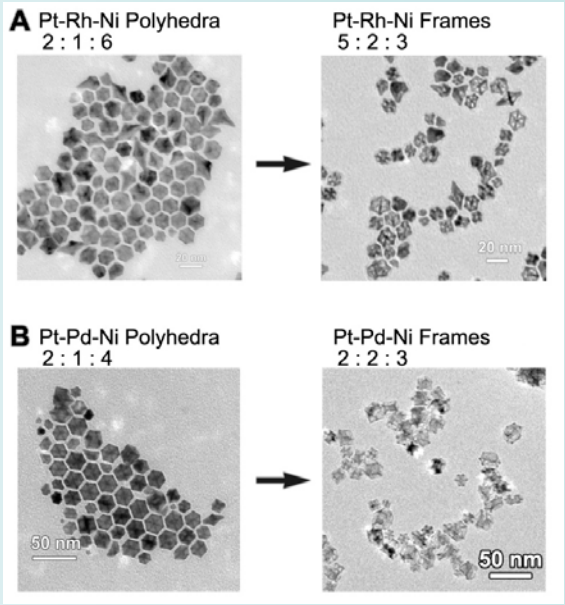
Accomplishments and Progress: *PtNi Nanoframes*

Incorporation of Ionic Liquid Into the Nanoframes





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



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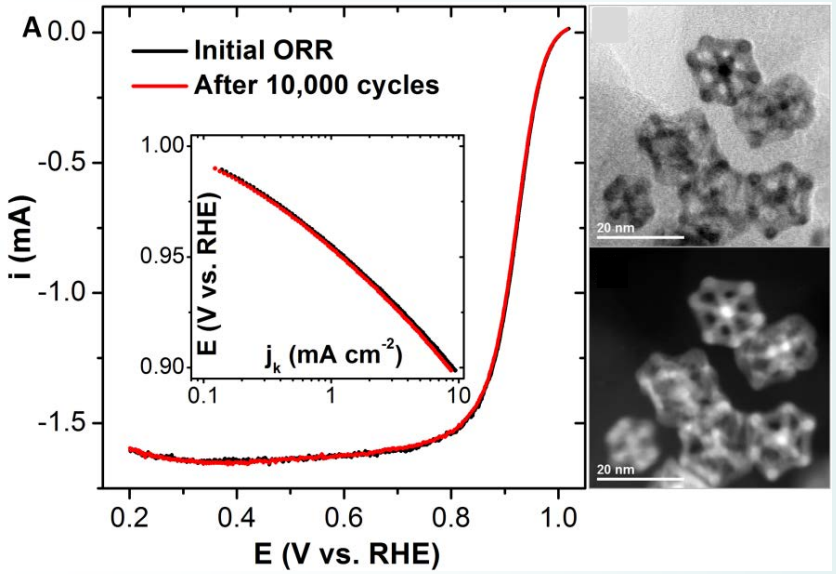
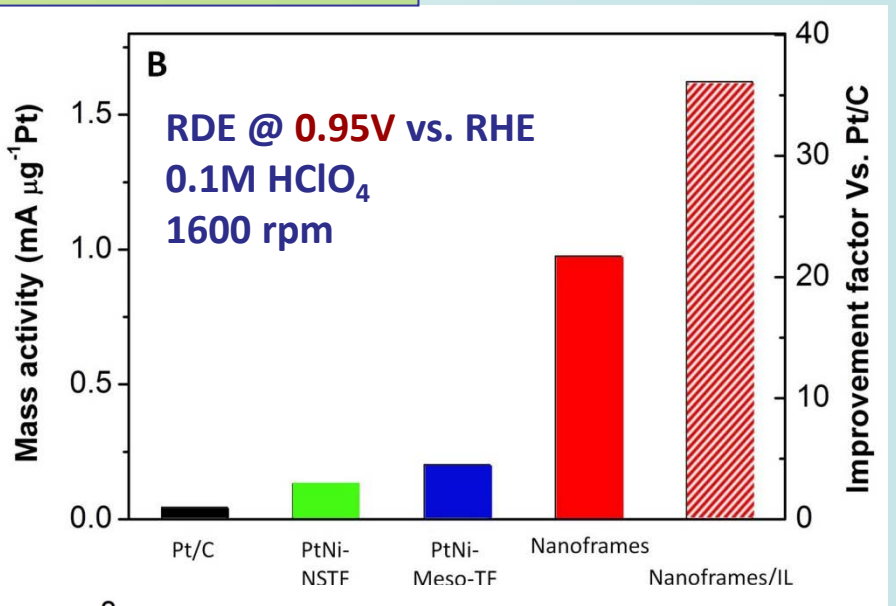
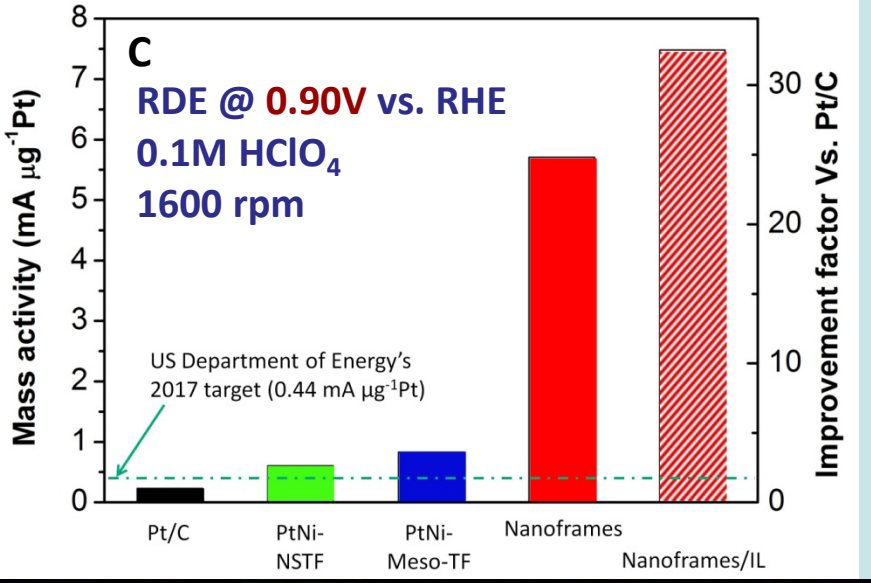
Accomplishments and Progress: *PtNi Nanoframes*

Electrochemical Evaluation of Nanoframes

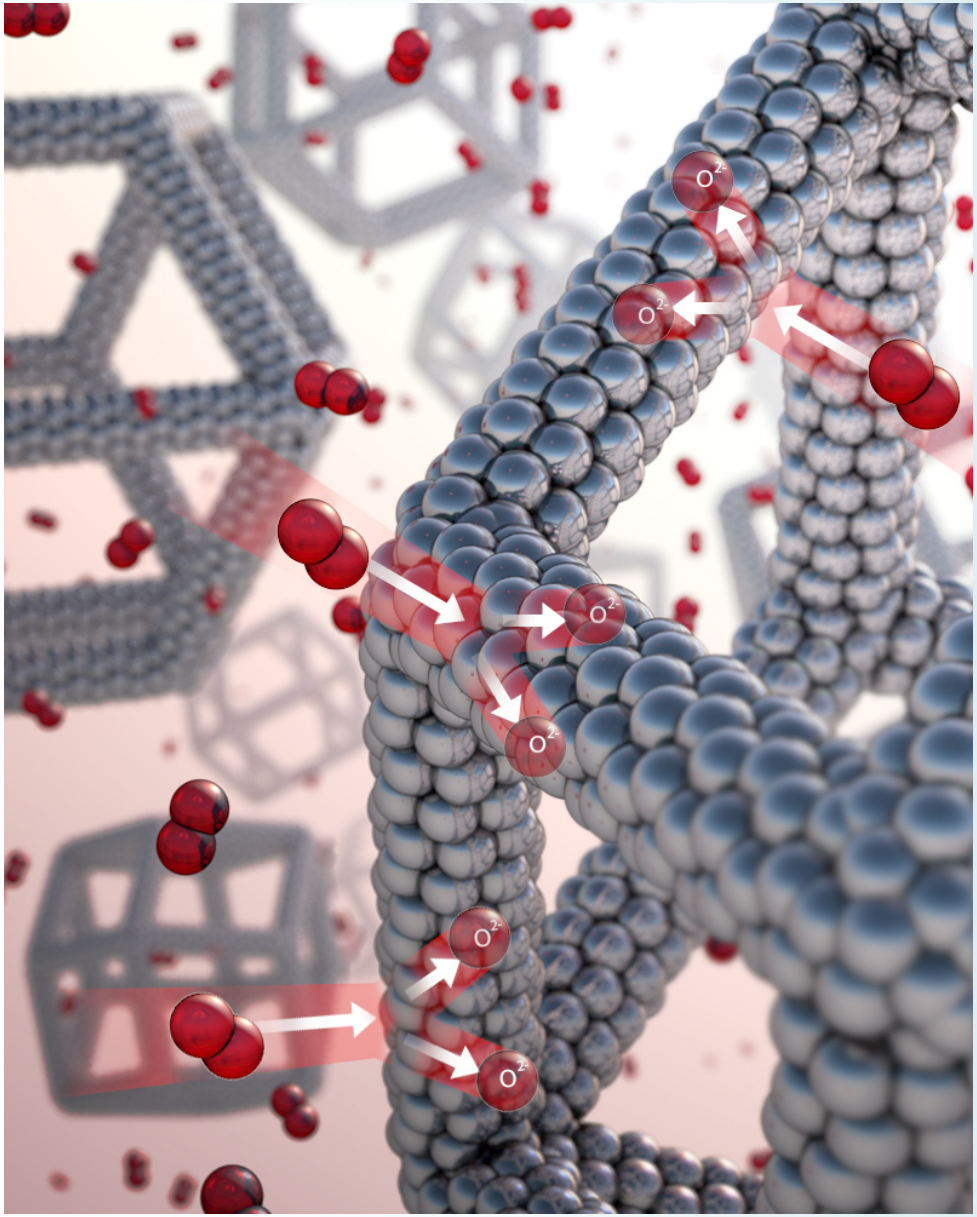


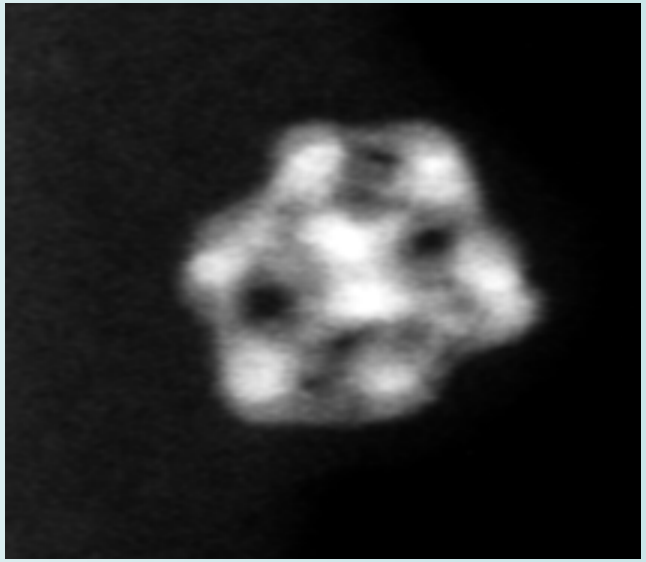


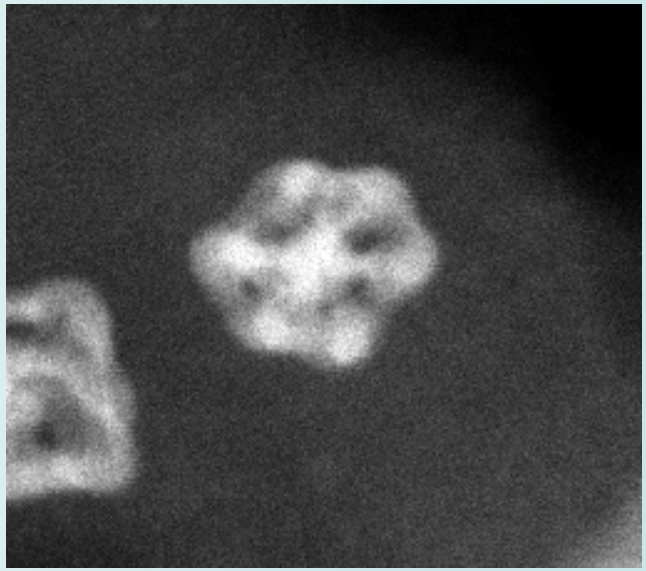


- No change in activity after 10K cycles 0.6 – 1.0 V
- Specific activity increase over 20-fold vs. Pt/C
- Mass activity increase over 35-fold vs. Pt/C
- Increase in mass activity over 15-fold vs. DOE target

Accomplishments and Progress: *Nanoframes – Principle of Operations*

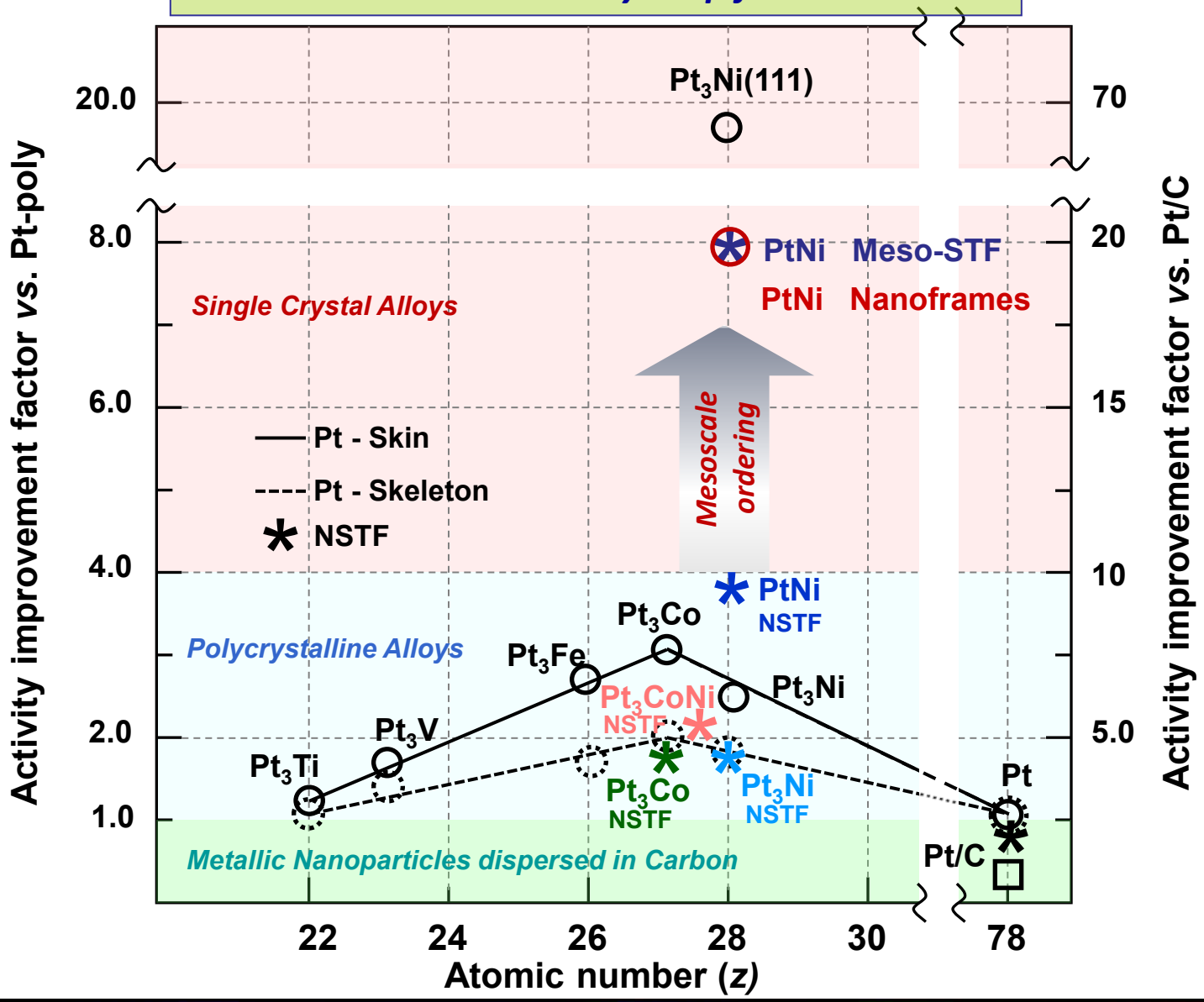






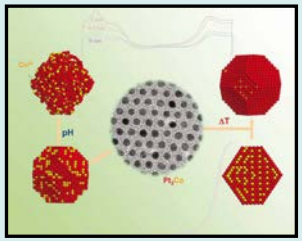
Accomplishments and Progress: *ORR on Pt-alloys*

Electrochemical Activity Map for the ORR



Summary

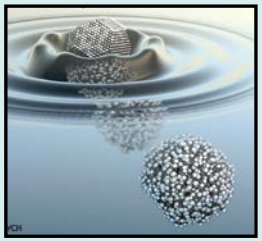
Electrocatalysts based on nanosegregated Pt alloy NPs, NWs, MSTFs and Nanoframes



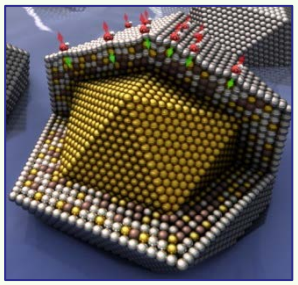
Efficient implantation of fundamental principles to the practical systems in the form of NPs, NWs, and nanoframes with adjustable compositional profile and structure

Established methodology that is capable to form and determine the nanosegregated Pt-skin surfaces for different classes of electrocatalysts

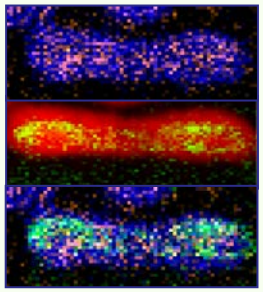
Established scalable synthetic protocols to produce larger amounts of materials



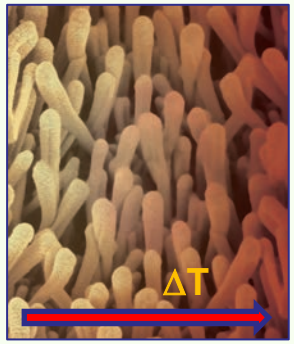
Evaluation of multimetallic Pt-alloy electrocatalysts



Different classes of materials have been synthesized in the form of NPs, NWs, nanoframes and characterized by TEM, HRSEM, in-situ HRTEM, XRD, RDE, MEA



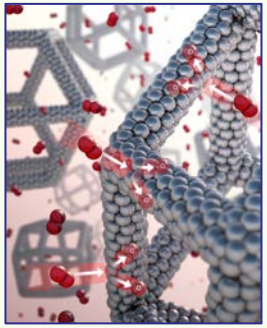
Specific activity of Pt-alloy vs. Pt/C electrocatalysts can be improved by 20-fold for Nanoframes and MSTF, 10-fold for core/shell NPs and 7-fold for NWs.
Mass activities improvements vs. Pt/C are 36-fold for nanoframes, 7-fold for core/shell, 6-fold for MSTF and 4-fold for NWs (RDE in 0.1M $HClO_4$ @ 0.95V *vs.* RHE)



Stability of Nanoframes, MSTF, core/shell NPs and NWs is superior compared to Pt/C

Two fold power of annealing facilitates the formation of an energetically more favorable surface state rich in (111) facets and distinct oscillatory segregation profile in core/shell NPs, NWs, mesostructured thin films and Nanoframes

Nanoframes are the first nanoscale catalyst with ORR bulk single crystal activity



Future Work

FY 2014

- Final tailoring of the composition that can provide activity/durability balance in Pt-alloys catalysts
- Synthesis and characterization of nanosegregated Pt-alloy nanoframe catalyst
- Optimization of the catalyst total metal loading
- Electrochemical evaluation of nanoframes in RDE and MEA (ANL, 3M)
- Scaling up of synthesis approach to produce larger quantities of the catalysts

FY 2015

- Activity/stability evaluation and optimization of MEA protocols at 3M, GM and ANL
- Achieving full capacity for scaling up of chemical synthesis of nanoframes supported on HSA carbon
- Alternative approaches for fabrication of nanoframe catalysts with ultra low PM content

Collaborations

SUB-CONTRACTORS

- **Oak Ridge National Laboratory** – HRTEM
- **Brown University** – Chemical Synthesis
- **University of Pittsburgh** (ex-Indiana University Purdue) – Theoretical Modeling
- **3M** – MEA Testing

COLLABORATORS

- **Argonne National Laboratory** – Nanoscale fabrication and DFT (CNM)
- **GM** – Technology transfer

Publications and Presentations FY09-14

14 Publications
32 Presentations
~650 Citations
2 issued US patents
3 patent applications

US 7,871,738 B2
Jan. 18, 2011

(54) **NANOSEGREGATED SURFACES AS CATALYSTS FOR FUEL CELLS**

(75) Inventors: **Vojislav Stamenkovic**, Naperville, IL (US); **Nenad M. Markovic**, Hinsdale, IL (US)

(73) Assignee: **UChicago Argonne, LLC**, Chicago, IL (US)

US 8,178,463 B2
May 15, 2012

(54) **HIGHLY DURABLE NANOSCALE ELECTROCATALYST BASED ON CORE SHELL PARTICLES**

(75) Inventors: **Vojislav Stamenkovic**, Naperville, IL (US); **Nenad M. Markovic**, Hinsdale, IL (US); **Chao Wang**, Chicago, IL (US); **Hideo Daimon**, Osaka (JP); **Shouheng Sun**, Providence, RI (US)

(73) Assignee: **UChicago Argonne, LLC**, Chicago, IL (US)