2013 DOE Hydrogen and Fuel Cells Program Review

Nanosegregated Cathode Catalysts with Ultra-Low Platinum Loading

Announcement No: DE-PS36-08GO98010

Topic: 1A

PIs: Nenad M. Markovic
Vojislav R. Stamenkovic

Materials Science Division

Argonne National Laboratory

Project ID# FC008

Overview

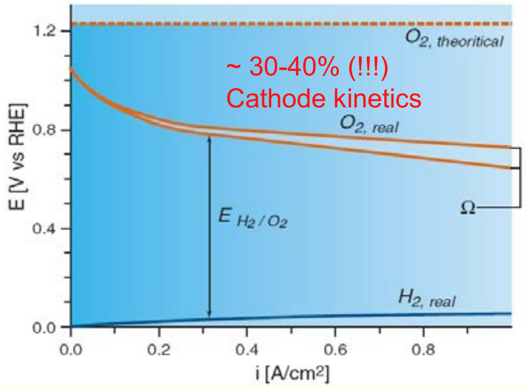
Timeline

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

Budget

- Total Project funding $ 3.6M
  - DOE share: 80 %
  - Contractor share: 20%
- Received in FY12: $ 700K
- Funding for FY13: $ 1.08M

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
- **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 and Fuel Cells Program is fundamental understanding of the oxygen reduction reaction on multimetallic systems of PtMN-alloys (M=Co,Ni; N=Fe, Mn, Cr, V, Ti etc) that will lead to the development of highly-efficient and durable *real-world nanosegregated Pt-skin catalysts with low-Pt content***

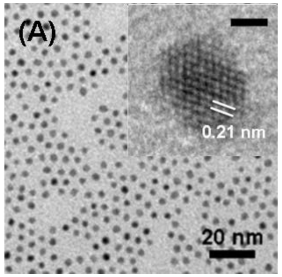
DOE Technical Targets

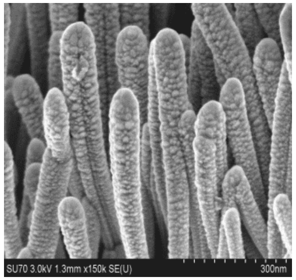
- Specific activity @0.9 $V_{iR\text{-}free}$: 720 $\mu A/cm^2$
- Mass activity @0.9 V: 0.44 A/mg_{Pt}
- Electrochemical area loss: < 40%
- Catalyst support loss: < 30%
- PGM Total content: 0.2 g/kW
- PGM Total loading: 0.2 $mg/cm^2_{electrode}$
- Cost*: $ 30/kW_e
- Durability w/cycling (80^oC): 5000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

*based on Pt cost of $450/troy ounce

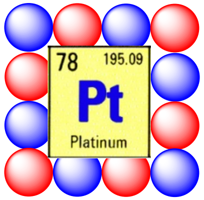
ANL Technical Targets

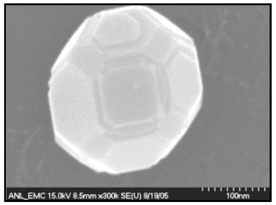
- Specific activity @ $0.9V_{iR\text{-}free}$
  2015 DOE target x 3
- Mass activity @ $0.9V_{iR\text{-}free}$
  2015 DOE target x 3
- Electrochemical area loss
  2015 DOE target
- PGM Total content
  < 0.1 g/kW

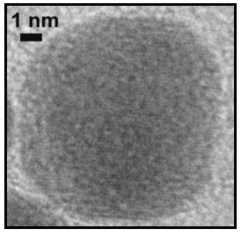




Approach







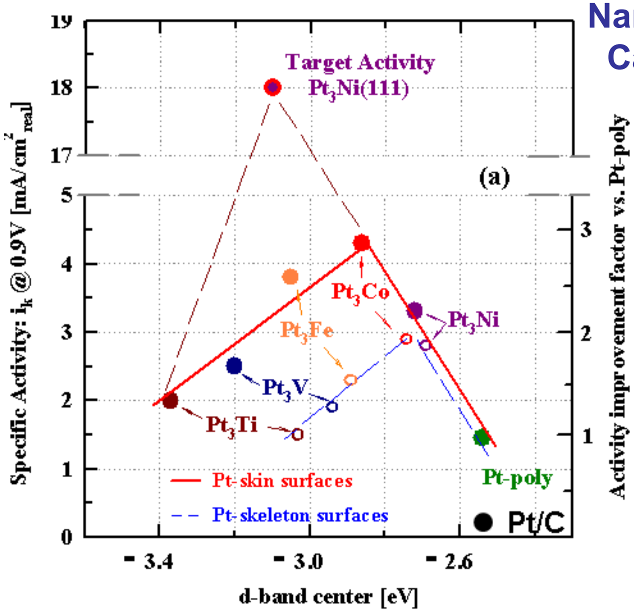
EXTENDED Multi-M SURFACES

THIN METAL FILMS / MODEL NANOPARTICLES

REAL NANOPARTICLES

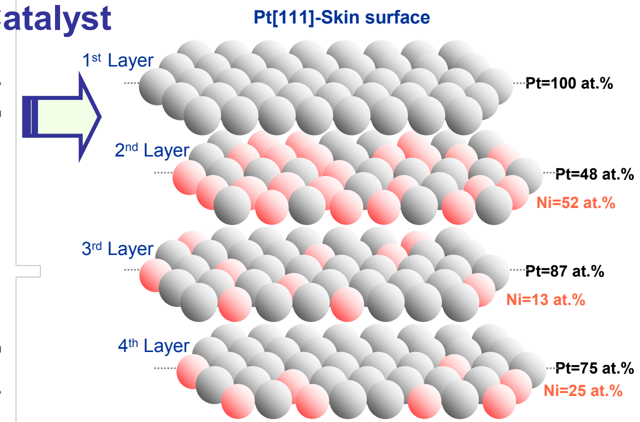
Materials-by-design approach - developed by ANL to design, characterize, understand, synthesize/fabricate and test advanced nanosegregated multi-metallic nanoparticles and nanostructured thin metal films

Well-Defined Systems



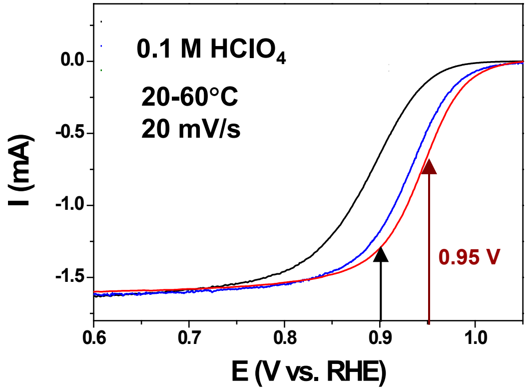
Advanced Nanoscale Catalyst

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

Approach / Milestone

(Go-No Go Decision Met)

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

1.1 Resolved electronic/atomic structure and segregation profile (95%)

1.2 Confirmed reaction mechanism of the ORR (100%)

1.3 Improved specific and mass activity (90%)

Milestone 2. Synthesis and characterization (FY10-13)

2.1 Physical methods: TM films (5-10 layers), nanoparticles (5-300 nm) (85%)

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

2.3 Characterization: Ex-situ (UHV, TEM) and in-situ (EXAFS, EC) (90%)

2.4 Theoretical modeling (DFT, MC) methods (90%)

Milestone 3. Fabrication and testing (FY11-13)

3.1 New PtM_1M_2 catalysts with higher activity and improved durability (90%)

3.2 Carbon support vs. nanostructured thin film catalysts (90%)

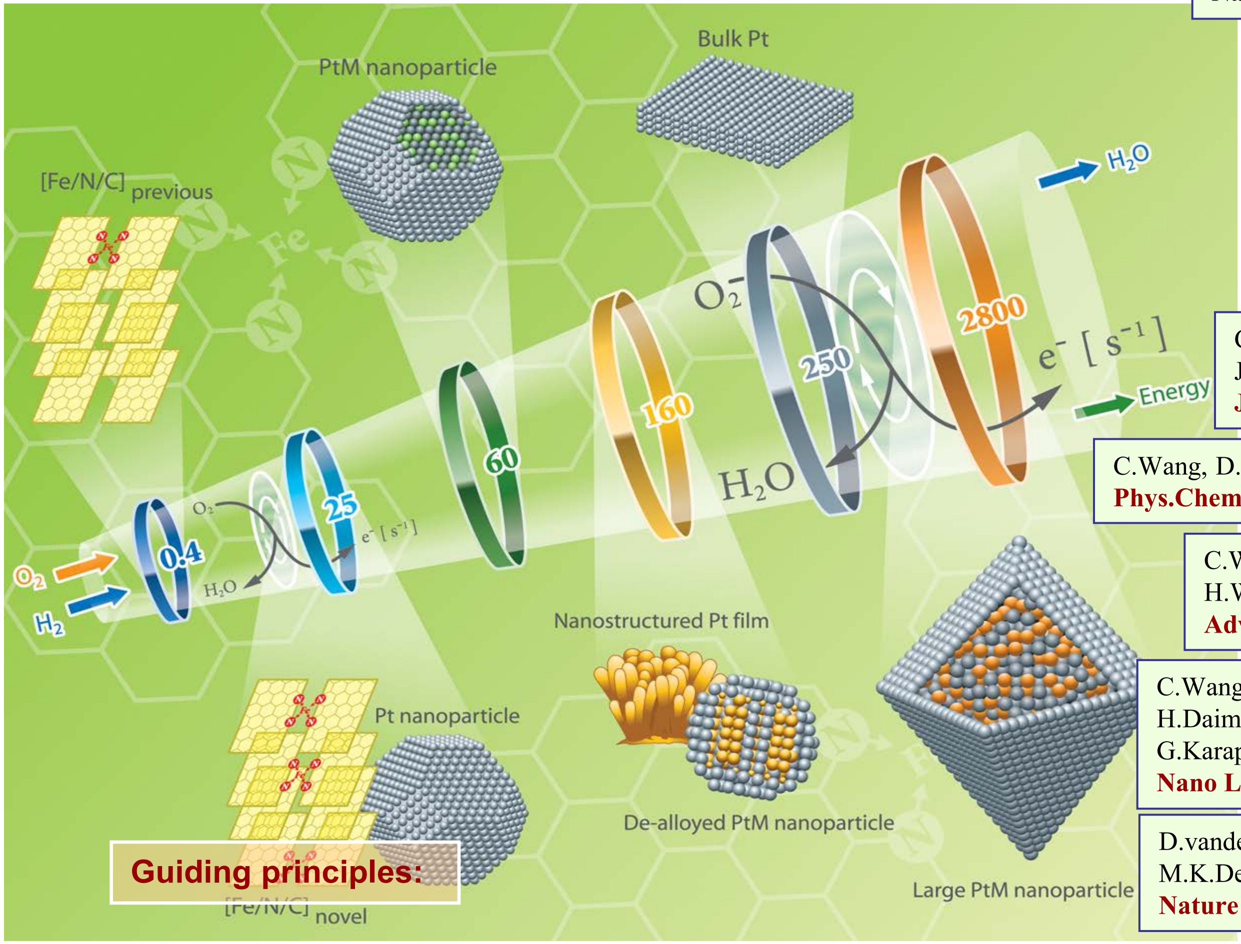
3.3 MEA testing (50 cm^2) of the optimized catalysts (45%)

3.4 Scale up of the catalyst fabrication in lab environment (50%)

Relevant Prior Work

Pt-alloy catalysts with nanosegregated concentration profile exhibit the superior performance for the ORR

- Maximization of activity by lowering the surface coverage of spectators
- Prevent leaching of TM by addition of Pt layers without activity loss
- Addition of the elements that may hinder Pt disolution



Guiding principles:

Selected publications from our group

V.Stamenkovic, B.S.Mun, K.J.J.Mayrhofer, P.N.Ross, N.M.Markovic
J. Am.Chem.Soc., 128(2006)8813

V.Stamenkovic, B.S.Mun, K.J.J.Mayrhofer, P.N.Ross, N.M.Markovic, J.Rossmeisl, J.Greeley, J.K. Norskov
Angew.Chem.Int.Ed., 45(2006)2897

V.Stamenkovic, B.S.Mun, M. Arenz, K.J.J.Mayerhofer, C.Lucas, G.Wang, P.N.Ross, N.M.Markovic
Nature Materials, 6(2007)241

V.Stamenkovic, B.Flower, B.S.Mun, G.Wang, P.N.Ross, C.Lucas, N.M.Markovic
Science, 315(2007)493

H.A. Gasteiger, N.M.Markovic
Science, 3124(2009)48

Selected publications from FY09-13

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

C.Wang, D.vanderVliet, K.C.Chang, N.M.Markovic, V.R.Stamenkovic
Phys.Chem.Chem.Phys., 12(2010)6933, COVER PAGE Article

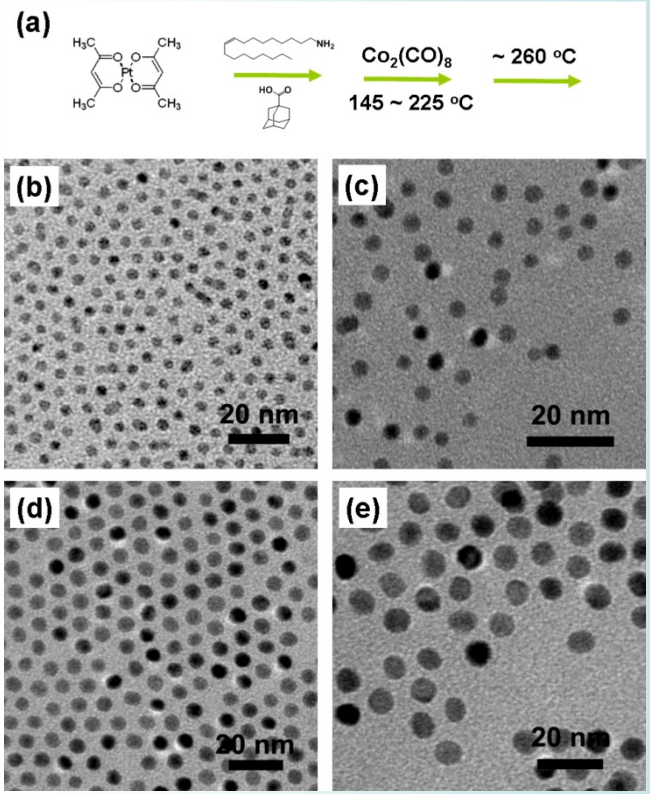
C.Wang, M.Chi, G.Wang, D.vanderVliet, D.Li, K.L.More, H.Wang, J.A.Schluter, N.M.Markovic, V.R.Stamenkovic
Adv. Funct. Mater. 21(2011)147, COVER PAGE Article

C.Wang, D.vanderVliet, K.L.More, N.J.Zaluzec, S.Peng, S.Sun, H.Daimon, G.Wang, J.Greeley, J.Pearson, A.P.Paulikas, G.Karapetrov, D.Strmcnik, N.M.Markovic, V.R.Stamenkovic
Nano Letters, 11(2011)919-928, COVER PAGE Article

D.vanderVliet, C.Wang, D.Tripkovic, D.Strmcnik, X.F.Zhang, M.K.Debe, R.T.Atanasoski, N.M.Markovic, V.R.Stamenkovic
Nature Materials, 11(2012)1051

Technical Accomplishments FY09 -12: *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

1° Particle size effect applies to Pt-bimetallic NPs

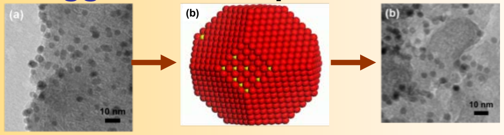
Specific Activity increases with particle size: 3 < 4.5 < 6 < 9 nm

Mass Activity decreases with particle size

Optimal size particle size ~5 nm

2° Temperature induced segregation in Pt-bimetallic NPs

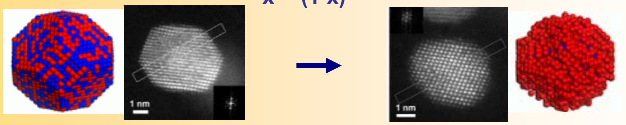
Agglomeration prevented



Optimized annealing temperature 400-500°C

3° Surface chemistry of homogeneous Pt-bimetallic NPs

$Pt_xM_{(1-x)}$ NPs



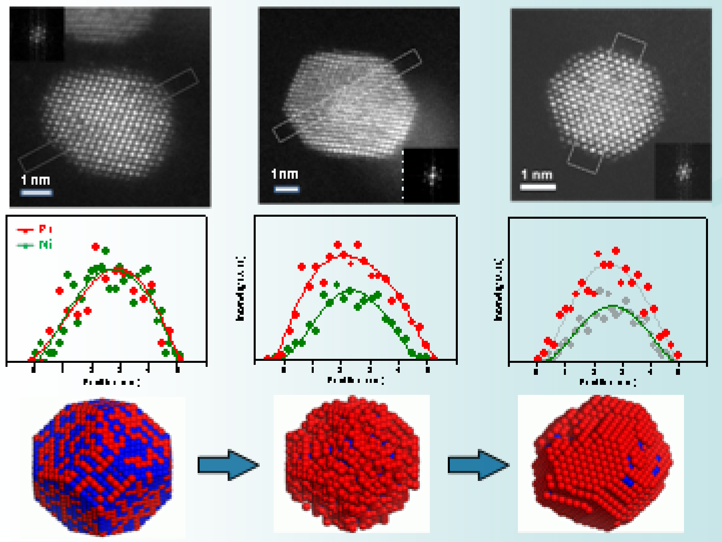
Dissolution of non Pt surface atoms leads to **Pt-skeleton** formation

4° Composition effect in Pt-bimetallic NPs

Pt_3M | PtM | PtM_2 | PtM_3

Optimal composition of Pt-bimetallic NPs is PtM

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

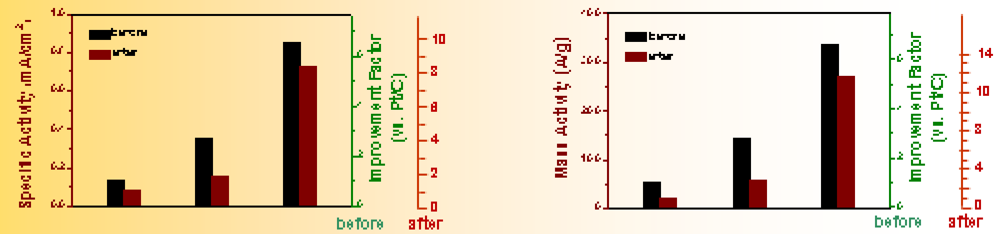


5⁰ Pt-bimetallic catalysts with mutilayered Pt-skin surfaces

Synthesized PtNi NPs have homogeneous distribution of Pt, Ni

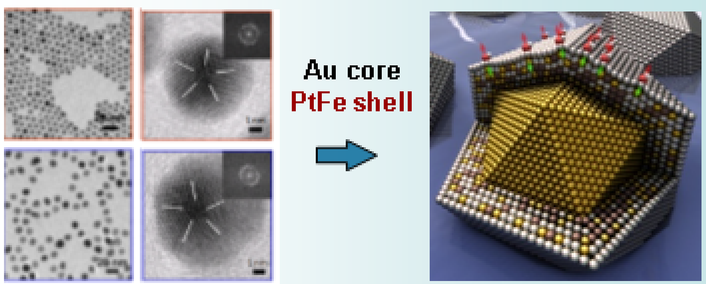
3-4ML of Pt-skeleton surfaces for PtNi acid leached NPs

Multilayered Pt-skin surfaces confirmed for PtNi annealed NPs

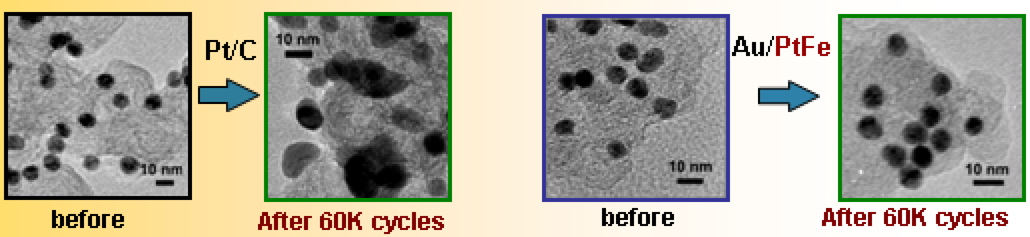


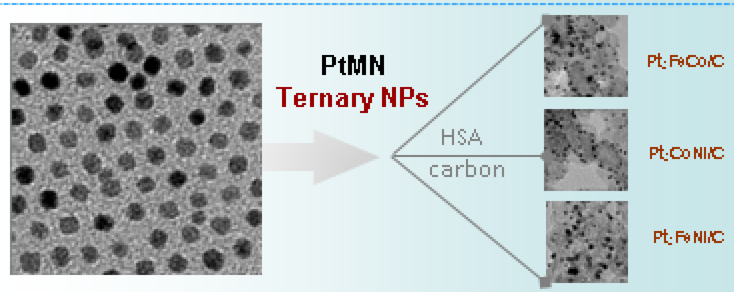
RDE after 4K cycles @60ºC (0.6-1.05V vs. RHE):

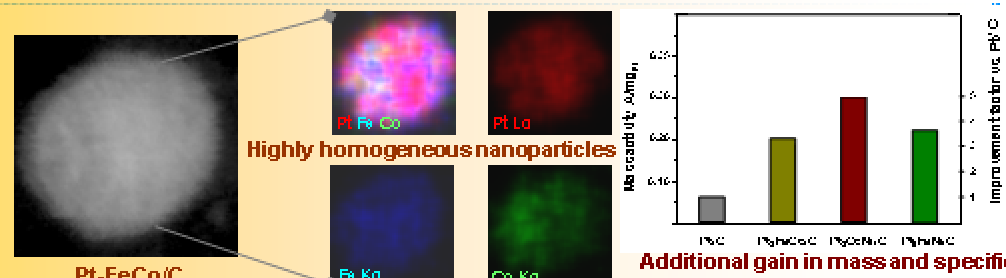
8-fold specific and 10-fold mass activity improvements over Pt/C



6⁰ Multimetallic NPs can further improve activity and durability

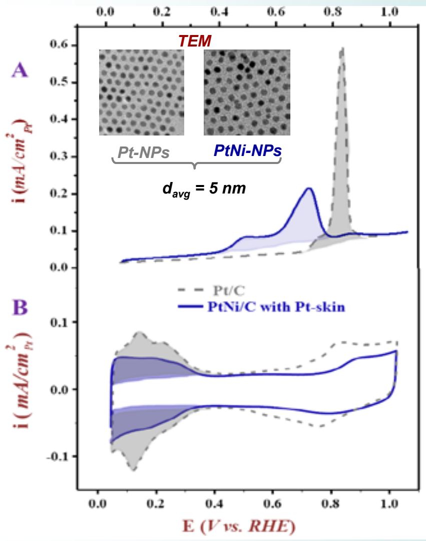


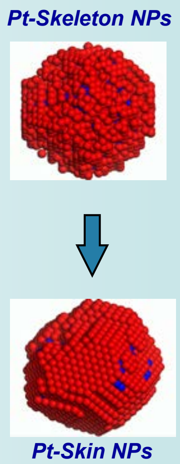




Additional gain in mass and specific activities vs. Pt and Pt_3M alloys

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





7° Electrochemically active surface area of Pt-skin catalysts

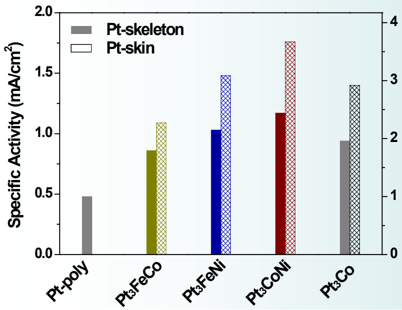
Catalysts with multilayered Pt-skin surfaces exhibit substantially lower coverage by H_{upd} vs. Pt/C (up to 40% lower H_{upd} region is obtained on Pt-Skin catalyst)

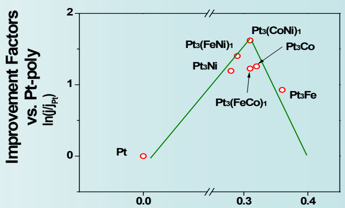
Surface coverage of adsorbed CO is not affected on Pt-skin surfaces

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

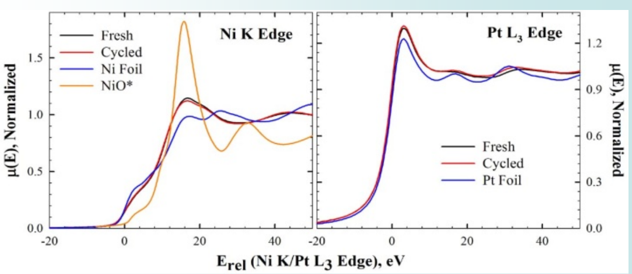




8° Multimetallic Pt_3NM alloys can further improve activity

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



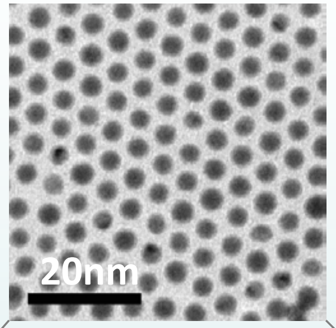
9° MEA: PtNi-MLSkin/NPs 20,000 potential cycles, 0.6 – 0.95 V

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

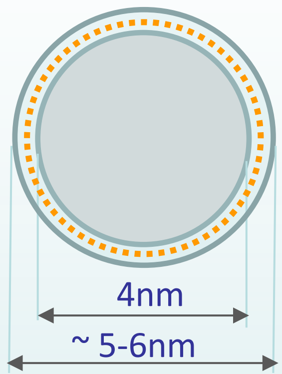
Specific surface area loss was only 12%, while Pt/C catalysts suffer loss of 20-50%

Technical Accomplishments: *Synthesis of Multimetallic Core Shell NPs*

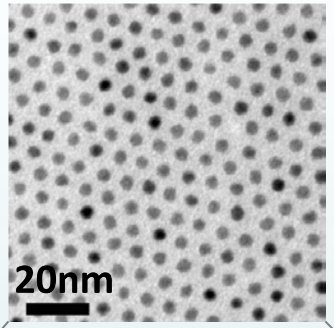
A



Ni seeds ~ 4 nm



B

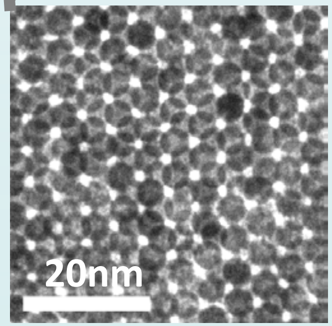


PtNi seeds ~ 4 nm

Pt:Ni = 30:70

1-2 layers of Pt

1º

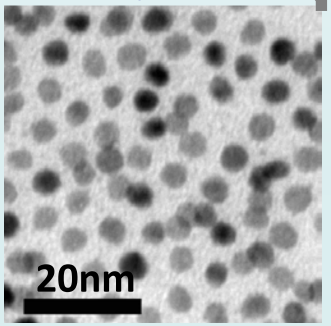


Ni@Pt ~ 4.5 nm

Ni:Pt = 40:60

~1 ML of Au
~1-2 layers of Pt

2º

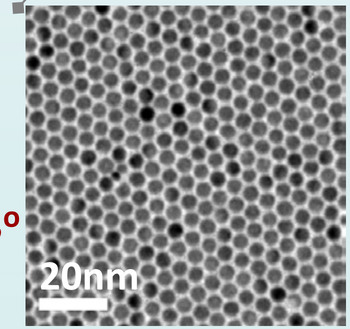


Ni@Au@Pt ~ 5 nm

Ni:Au:Pt = 33:30:37

1-2 layers of Pt

3º

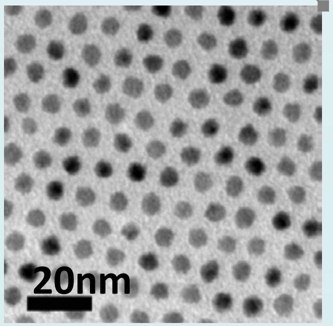


PtNi@Pt ~ 4.8 nm

Pt:Ni = 68:32

~1 ML of Au
~1-2 layers of Pt

4º

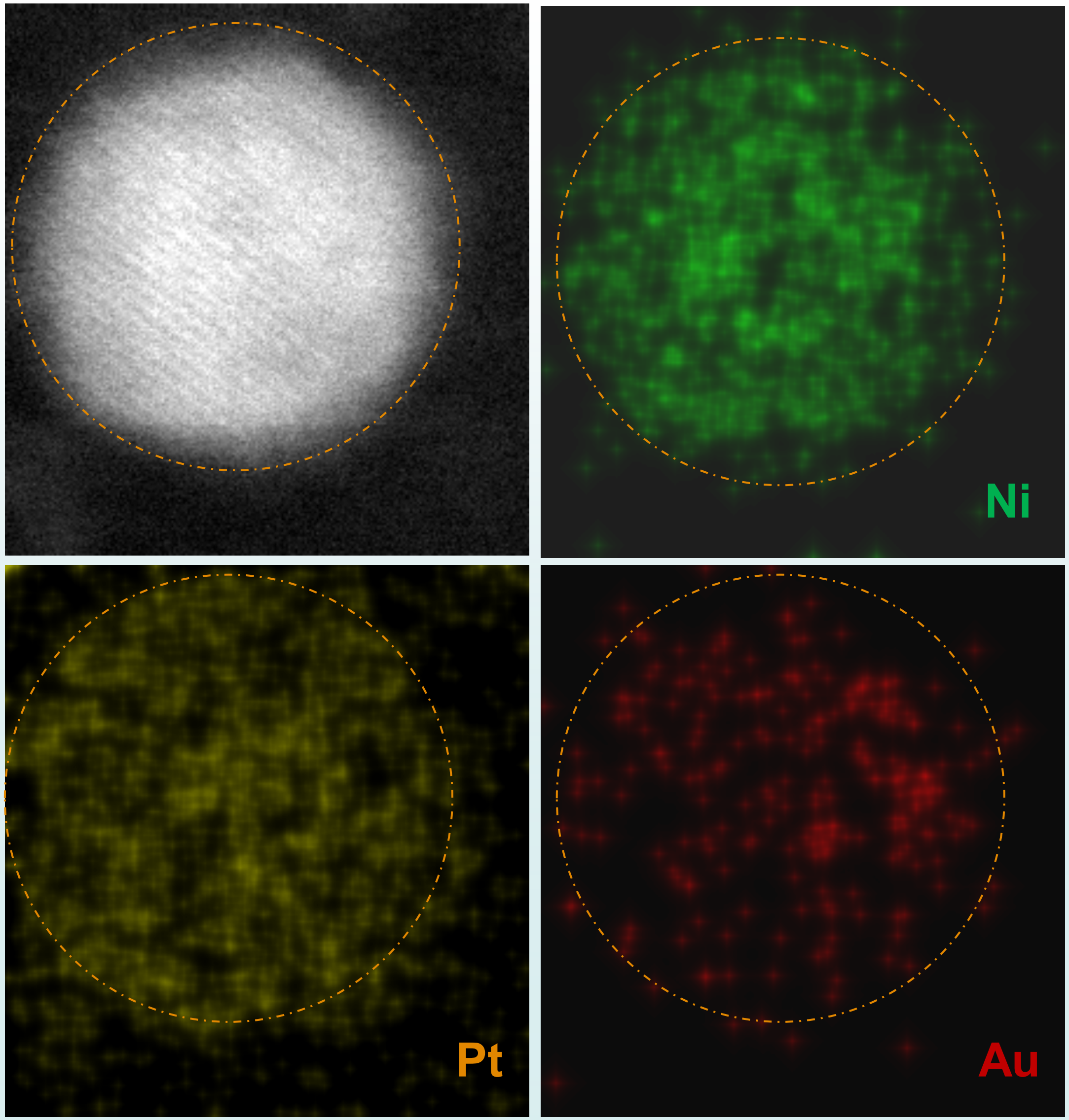


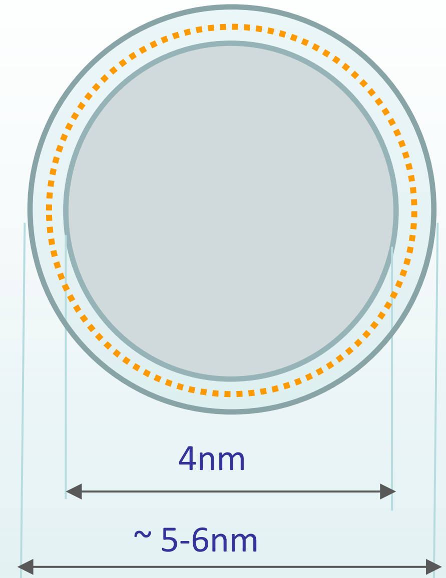
PtNi@Au@Pt ~ 6 nm

Pt:Ni:Au = 50:5:45

Technical Accomplishments: *Characterization of Core/Shell Ternary Alloy NPs*

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





EDS:

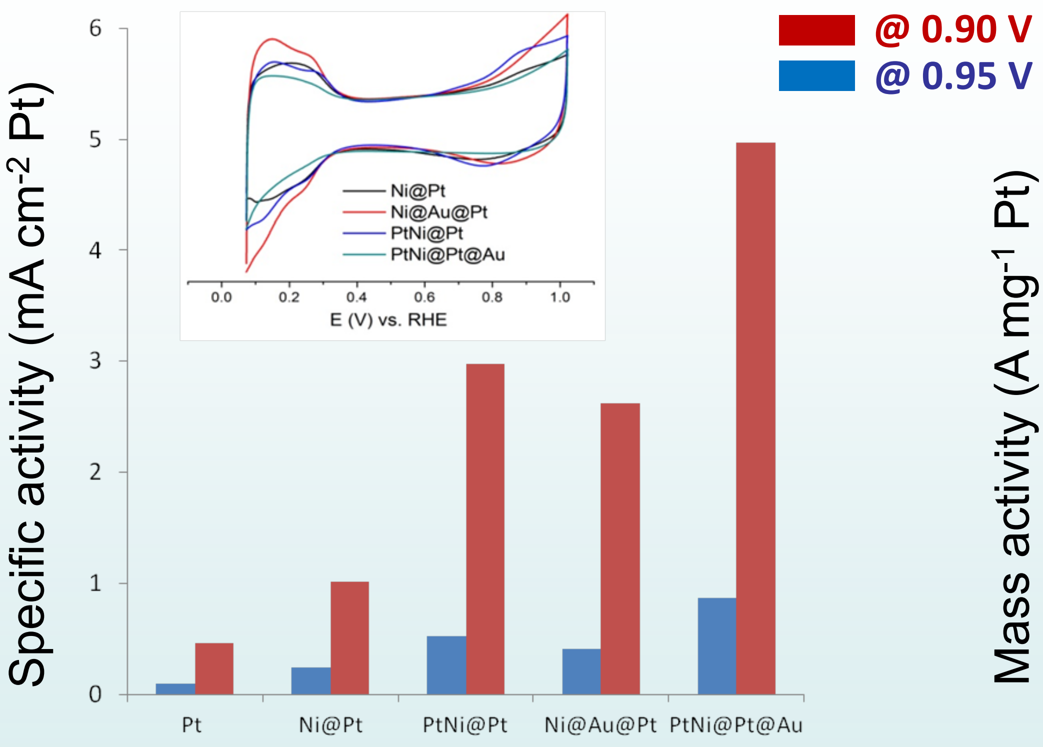
-Core/Shell concentration profile

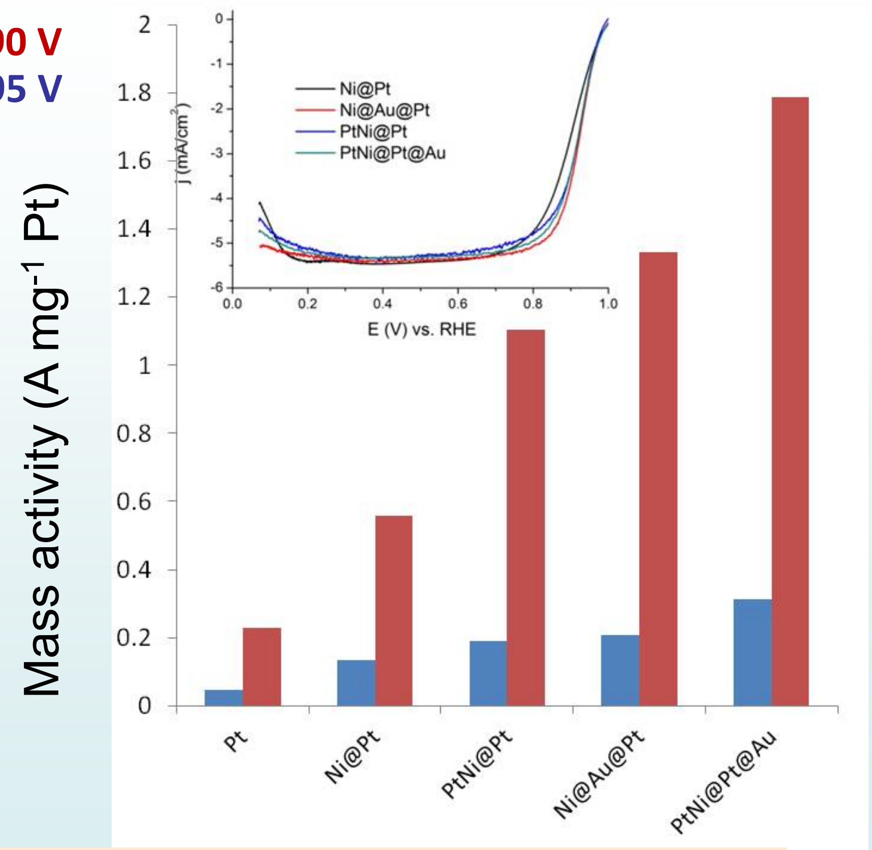
-Subsurface Au

-Uniform elemental distribution

Technical Accomplishments: *Characterization of Core/Shell Alloy NPs*

Electrochemical evaluation of Core/Shell NPs by RDE

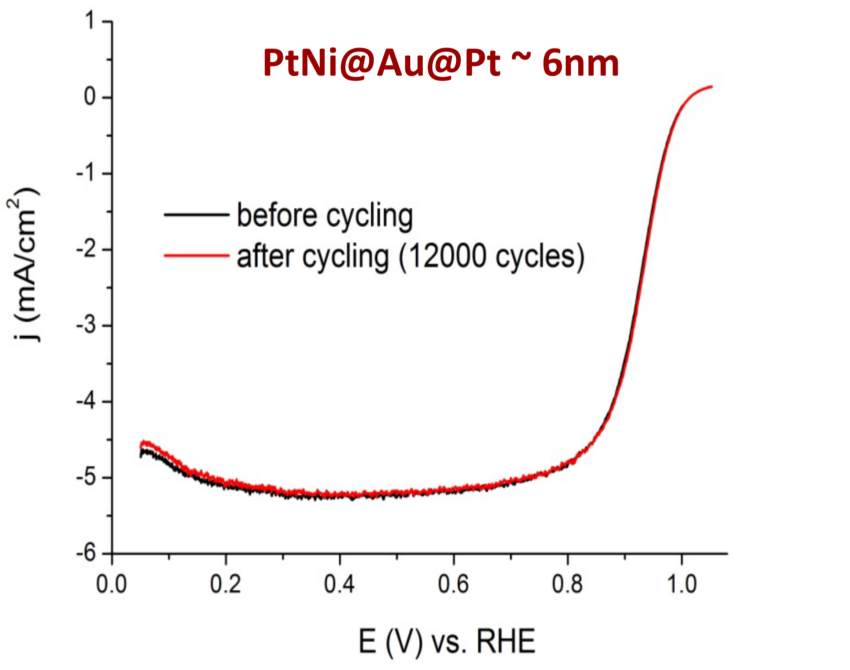


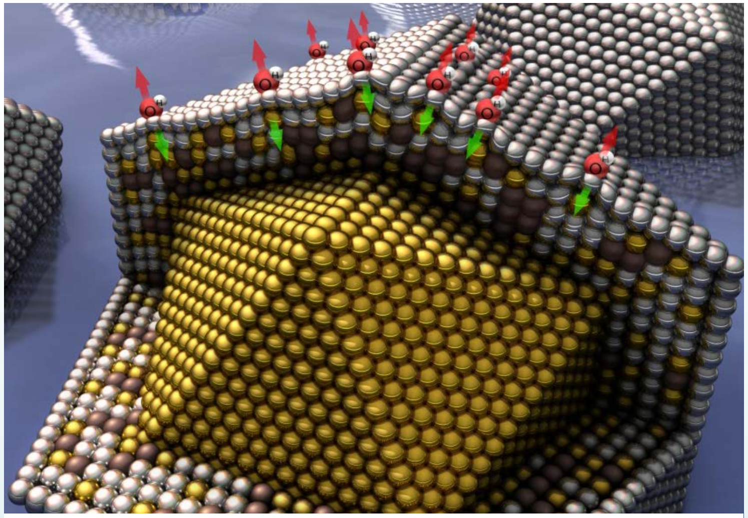


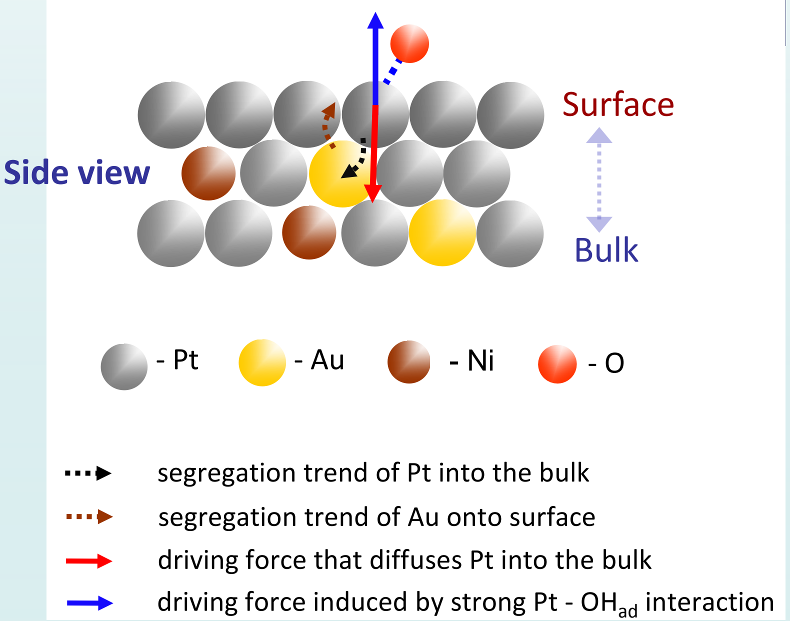
1. PtNi@Pt exhibits higher specific activity than Ni@Pt, although their overall compositions are similar, implying lattice mismatch may play an important role
2. Adding small amount of Au in between Ni and Pt increases the specific activity, compared to Ni@Pt, while the activity is not significantly lower than that of PtNi@Pt
3. Because Au and PtNi have similar lattice constant, it further confirms that lattice mismatch is important to tune the electrocatalyst activity

Technical Accomplishments: *Characterization of Core/Shell Alloy NPs*

Durability evaluation of PtNi/Au/Pt NPs by RDE





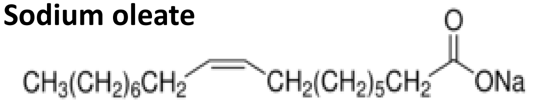


1. Core/Shell Alloy NPs are highly durable catalysts with no change in activity after 12,000 cycles
2. Subsurface layer of Au stabilizes topmost Pt atoms
3. Small amount of Au in between PtNi and Pt is preventing dissolution of Pt atoms due to the counterbalance between two opposing forces: Pt-OH interaction and Pt-Au
4. Subsurface Au also suppresses place exchange mechanism between Pt-O

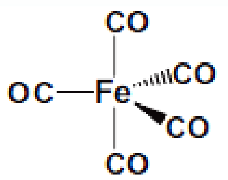
Technical Accomplishments: *Synthesis of Pt-Alloy Nanowires*

Sodium oleate
Oleylamine → 120°C → **Add $Fe(CO)_5$** → 240°C → **Add $Pt(acac)_z$** → 70°C → **Acid Treatment**

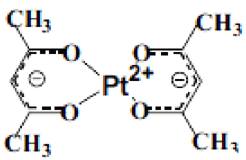
Sodium oleate



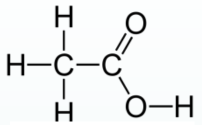
Oleylamine (OAm)



$Fe/Co(CO)_5$



$Pt(acac)_2$

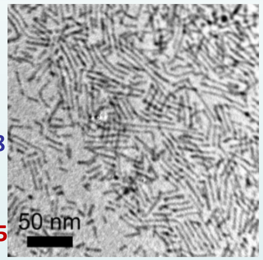


CH_3COOH
+
NWs

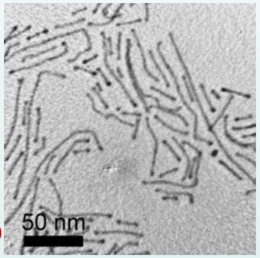
Composition Control:

Acid Treatment

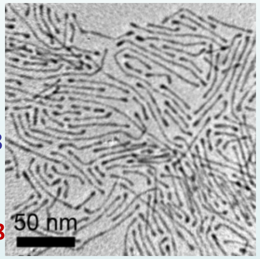
$Fe_{42}Pt_{58}$ → $Fe_{15}Pt_{85}$



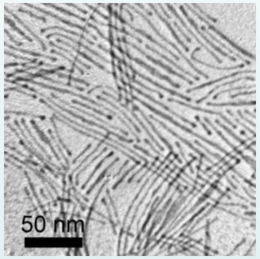
$Fe_{68}Pt_{32}$ → $Fe_{20}Pt_{80}$



$Co_{32}Pt_{68}$ → $Co_{12}Pt_{88}$

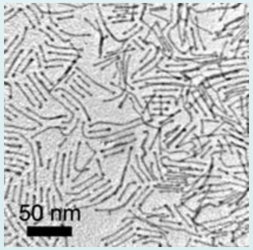


$Co_{63}Pt_{37}$ → Co_8Pt_{92}

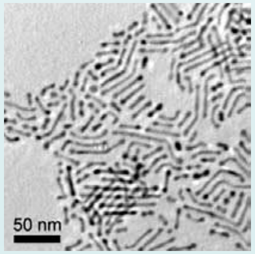


Width Control:

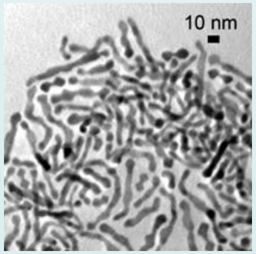
2.5 nm



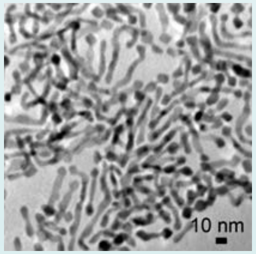
3.7 nm



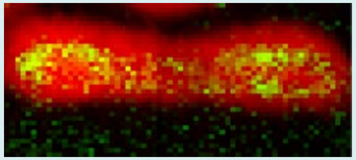
5.5 nm



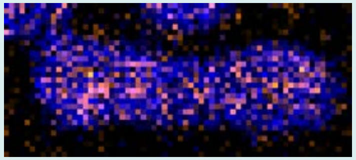
6.3 nm



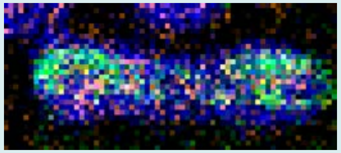
Segregation Profile Control:



FePt@Pd



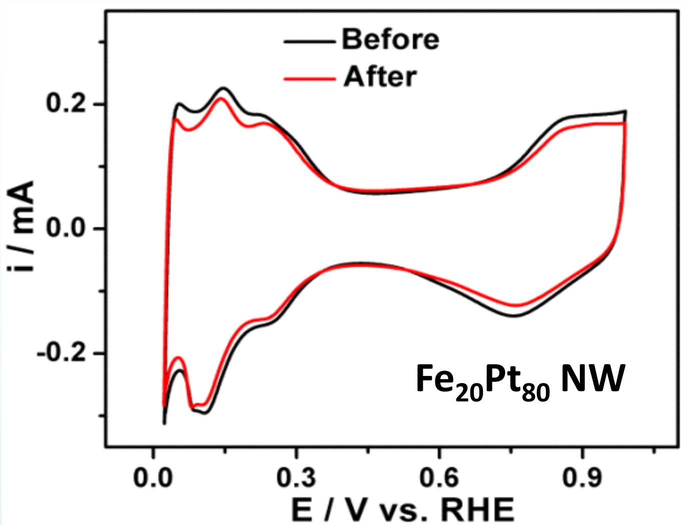
FePt@Pd@FePt

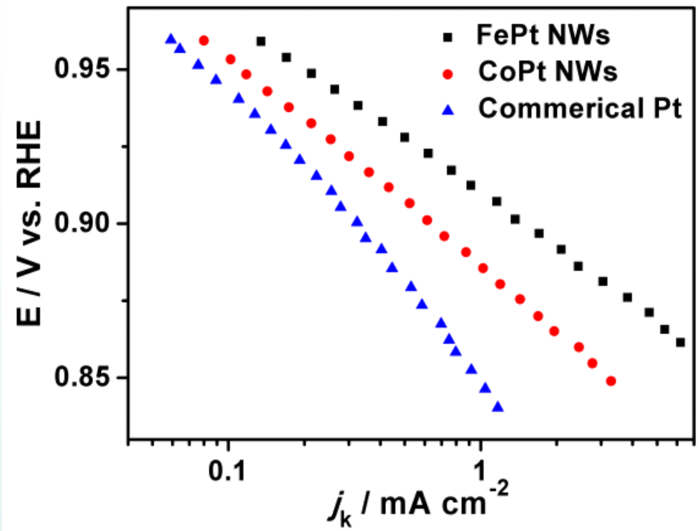


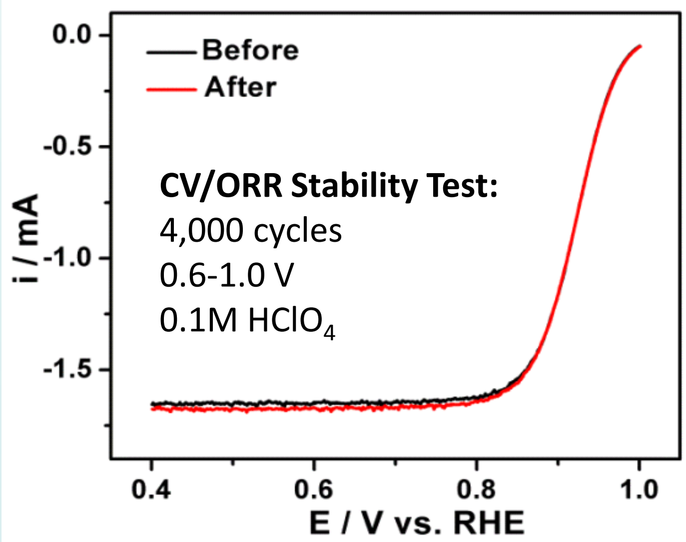
FePt@Au@FePt

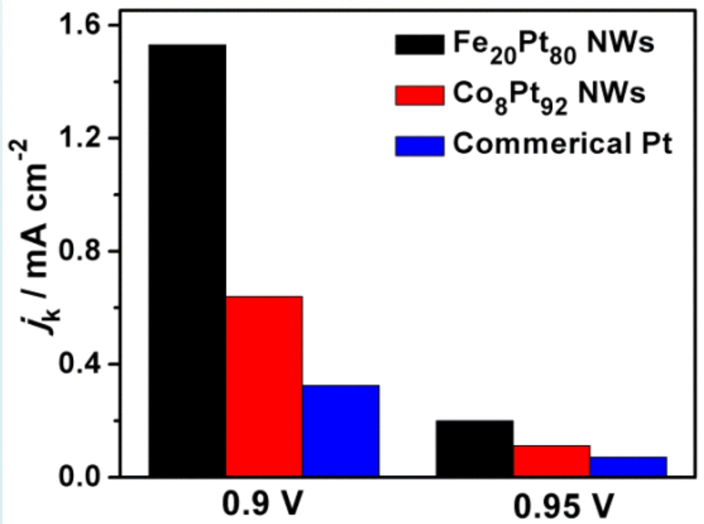
Technical Accomplishments: *Characterization of Alloy NWs*

Electrochemical evaluation of Alloy NWs by RDE





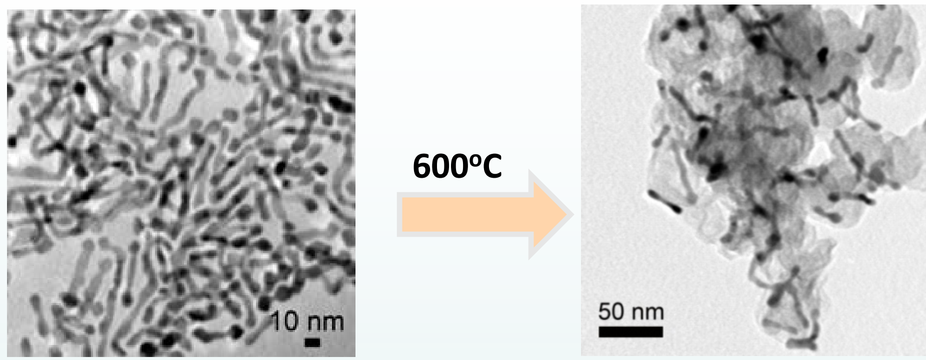


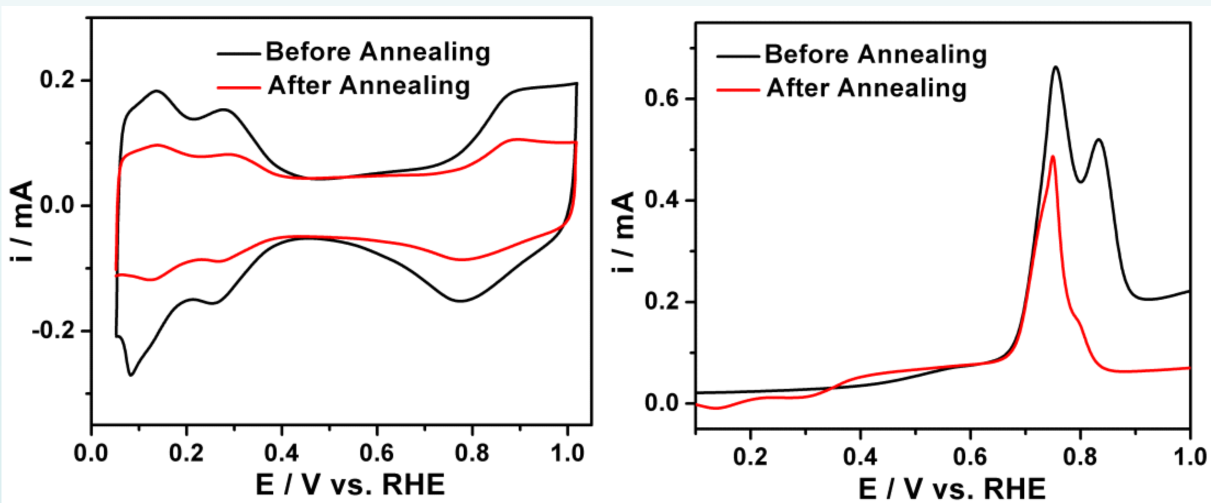


SA: 1.53 mA/cm^2 and MA: 0.85 A/mg$_{Pt}$ / The best NW catalysts for ORR to date

Technical Accomplishments: *Annealing of Pt-alloy NWs*

Formation of Pt-Skin over Pt-alloy NWs





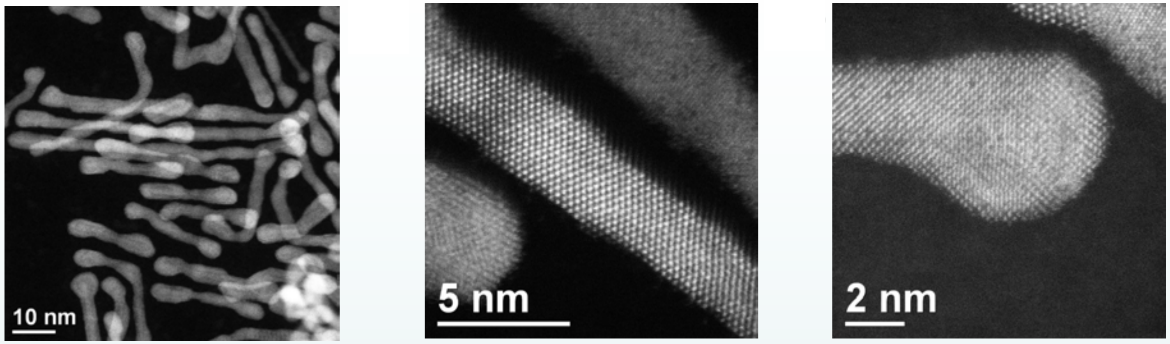
	Pt/C	FePt NW/C	FePt NW/C Annealed
ECSA(CO_{ad})/ ECSA(H_{upd})	1.00	1.05	1.3

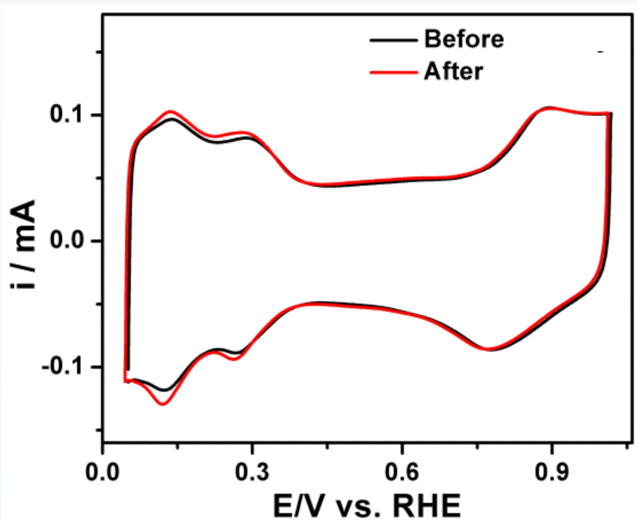
Pt – Skin is formed over FePt MW:

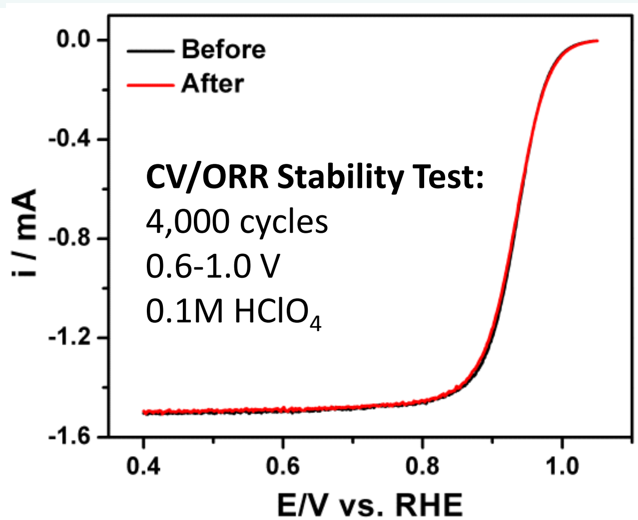
Suppressed H_{upd} region
The positive shift of the $[Pt\text{-}OH]_{ad}$ peak
The ratio between H_{upd}/CO stripping charge > 1

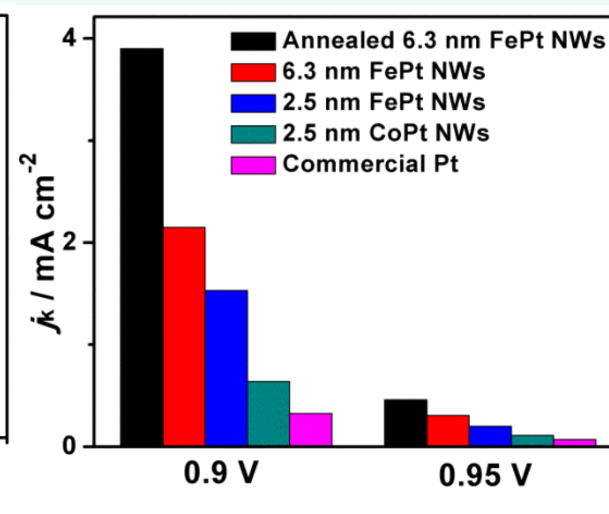
Technical Accomplishments: *Annealed Pt Alloy NWs*

Electrochemical evaluation of Pt-alloy NWs by RDE









1. Pt Alloy NWs are active and highly durable catalysts with no change in activity after 4,000 cycles
2. Specific activity depends on the composition and width of NWs
3. Annealing of NWs induces formation of nanosegregated profile with Pt-skin type of surface
4. Pt-skin confirmed by suppressed H_{upd}, Pt-OH shift, CO_{ad}/H_{upd} ratio, and high activity for the ORR

Mesostructured Thin Films as Electrocatalysts

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 crystalline systems in thin film materials

Research Details

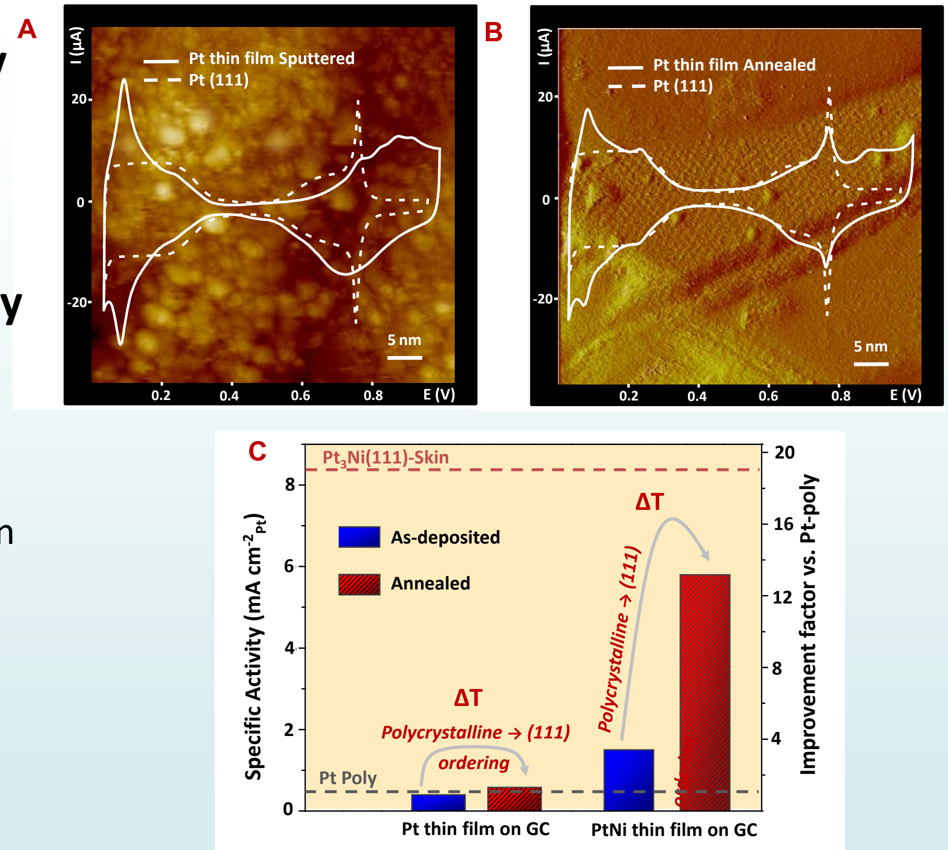
–Nanostructured surface morphology of sputtered thin metal films is transferred into mesostructured surface with single crystalline properties

–Individual randomly oriented nanoscale grains coalesce and form large interconnected well-ordered (111) facets

–Superior catalytic activity for the oxygen reduction reaction of extended $Pt_3Ni(111)$ single crystalline surface has been achieved in mesostructured thin films

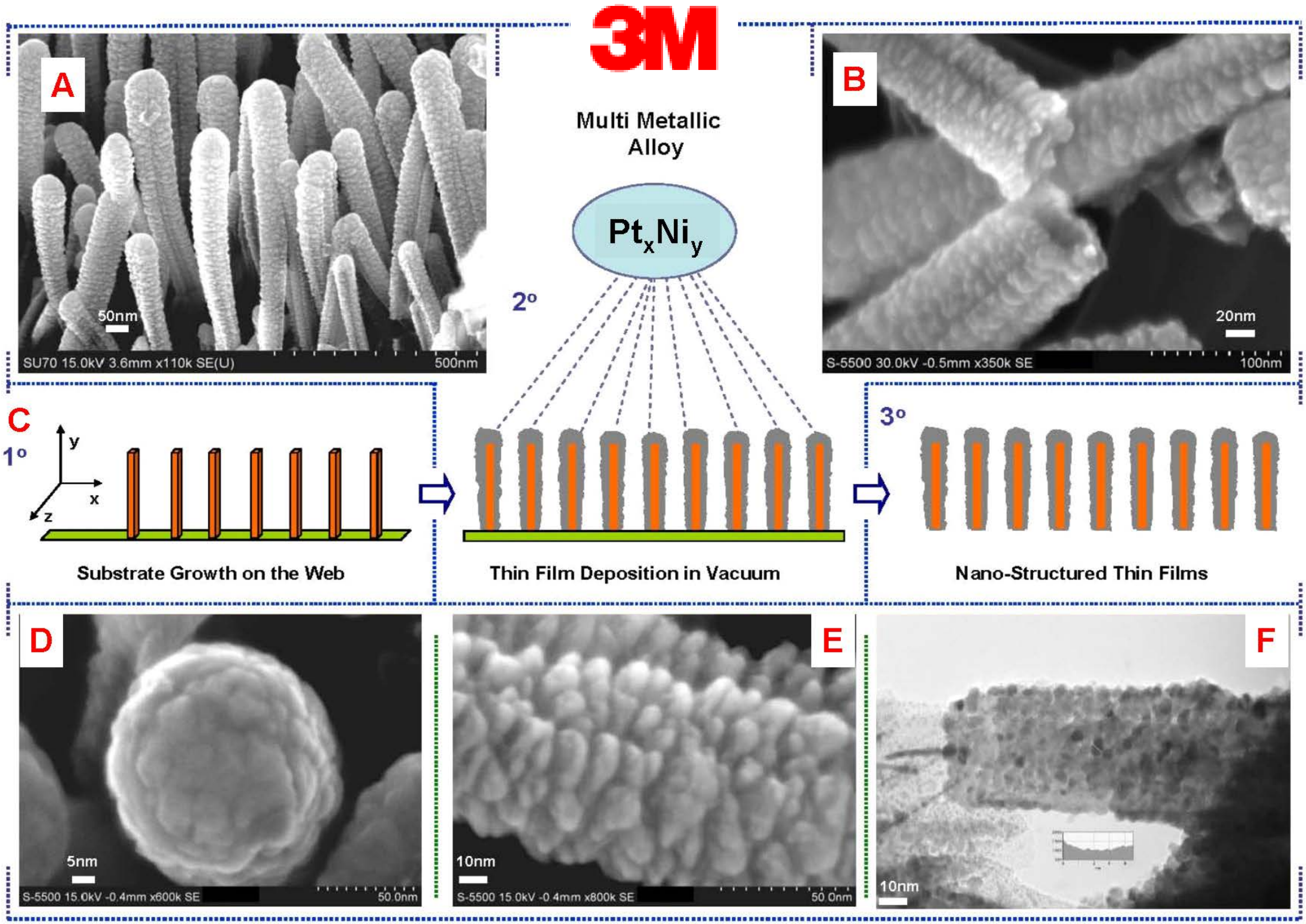
D.F. vander Vliet, C. Wang, D. Tripkovic, D. Strmcnik, X. Zhang, M.K. Debe, R.T. Atanasoski, N.M. Markovic and V.R. Stamenkovic

Nature Materials, (2012), DOI:10.1038/NMAT3457

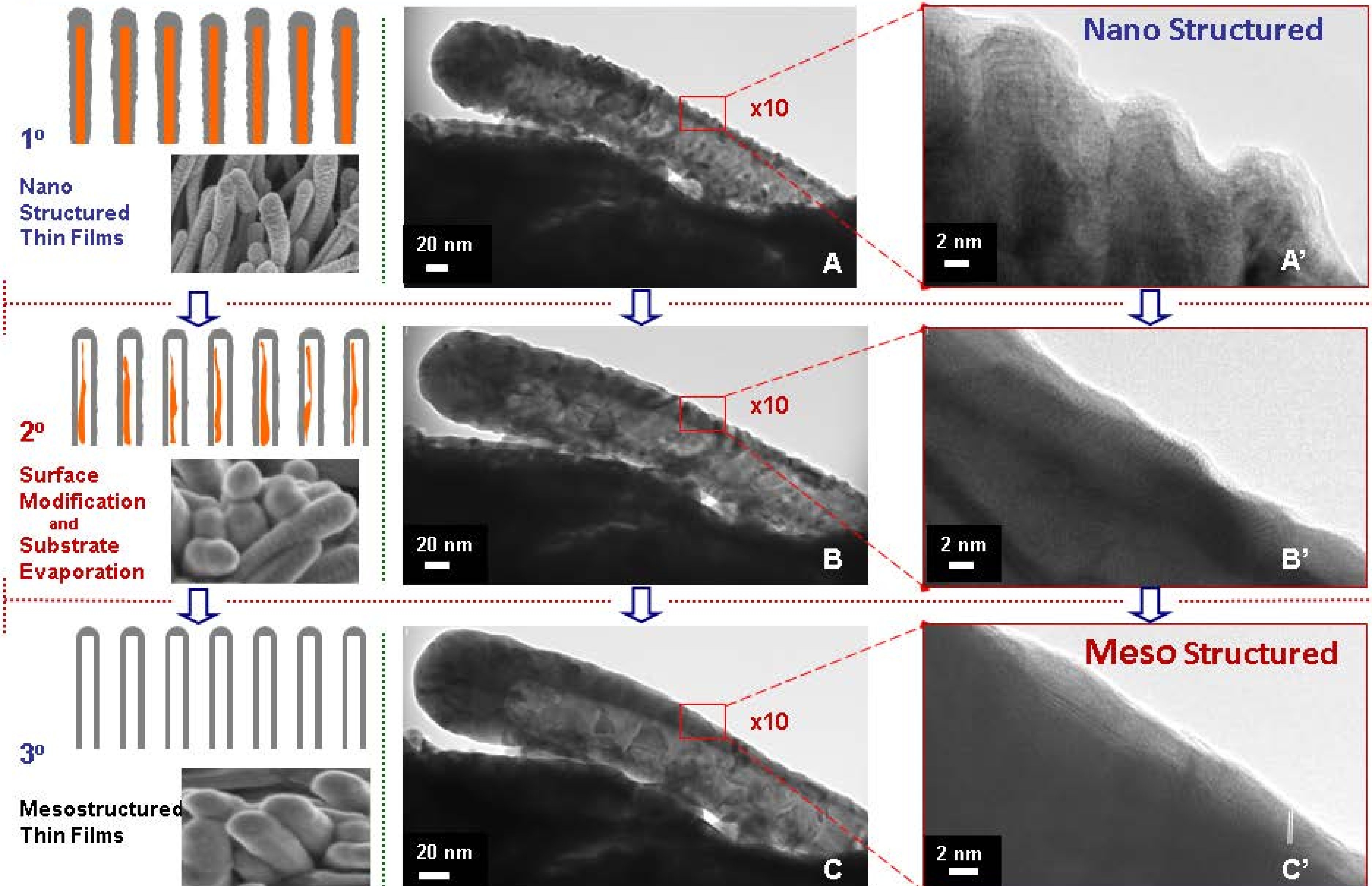


Tuning of the thin film surface morphology and structure: Cyclic voltammetry and STM images of Pt and Pt alloy thin films deposited on a glassy carbon (GC) substrate: **(A)** as-deposited Pt thin film and Pt(111), **(B)** annealed Pt thin film and Pt(111), **(C)** specific activities for the ORR of Pt and PtNi thin films with improvements factors *vs.* polycrystalline Pt surface

Technical Accomplishments: *NSTF Surface Morphology Characterizaion*

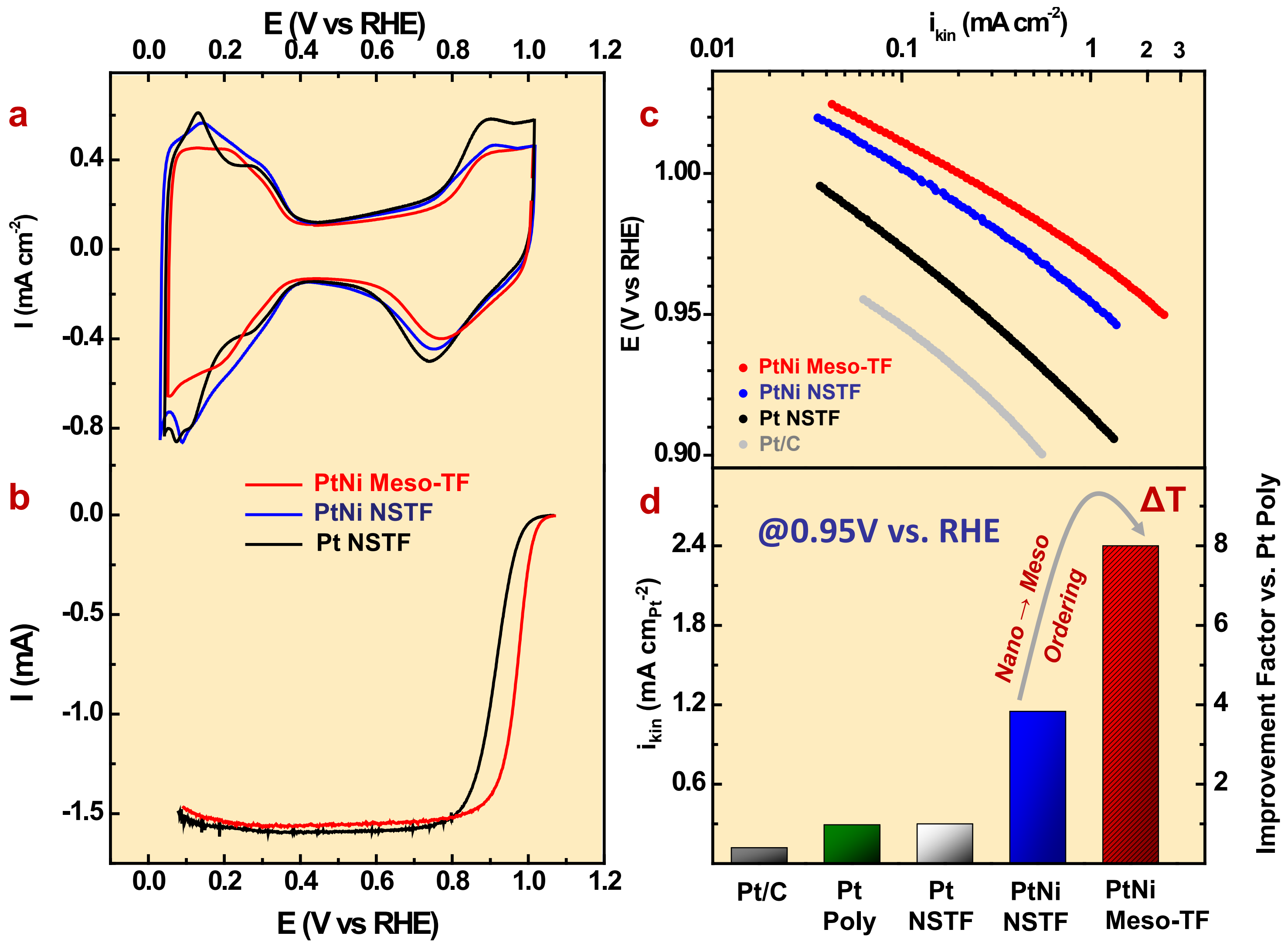


Technical Accomplishments: *Tuning of the Thin Film Surface Morphology*



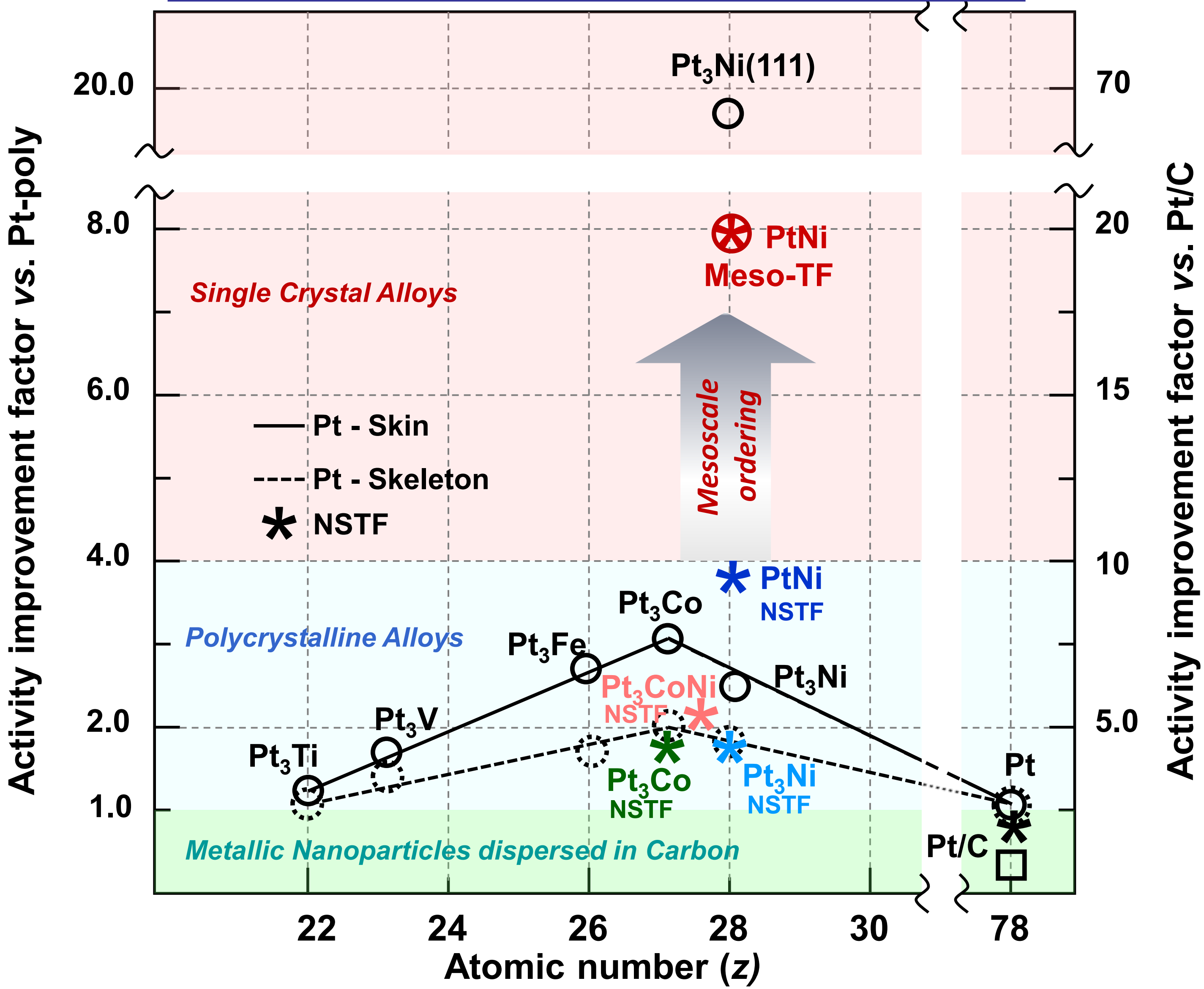
Technical Accomplishments: *Characterization of MSTF*

Electrochemical evaluation of MSTF by RDE



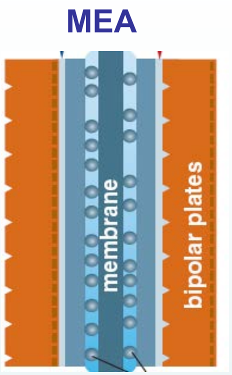
Technical Accomplishments: *ORR on MSTF*

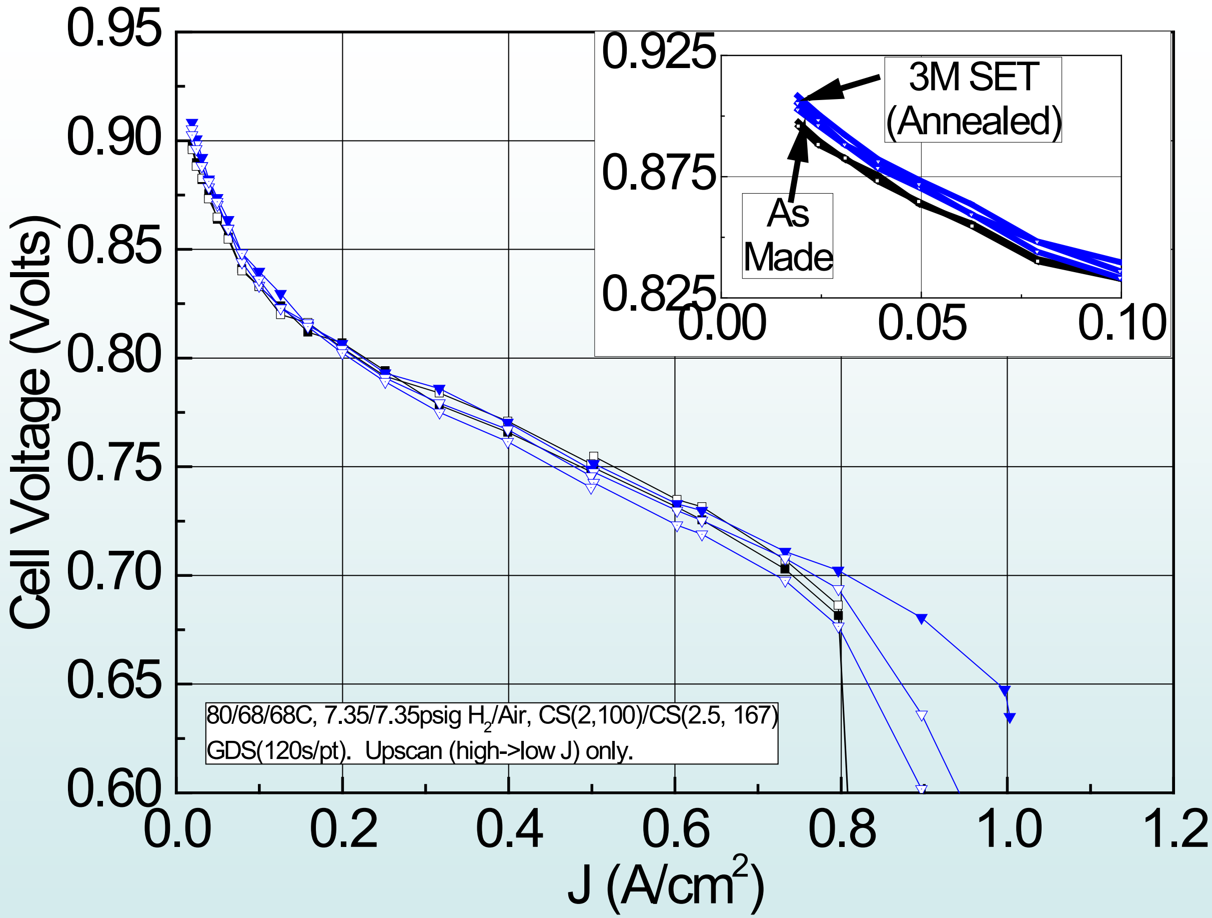
Electrochemical Activity Map for the ORR



Technical Accomplishments: *MSTF Catalyst*

MEA Studies of Mesostructured Thin Film Catalyst





Anode: 0.05PtCoMn/NSTF. Cathode: 0.125PtNi/NSTF. PEM: 3M 24µ 825EW

3M Surface Energetic Treatment (SET) increases ORR kinetics of PtNi/NSTF by ~20mV as measured under H_2/Air Polarization in MEA

Summary

Electrocatalysts based on nanosegregated Pt alloy NPs, NWs and MSTF:

- Efficient implantation of fundamental principles to the practical systems in the form of NPs, NWs and thin metal films with adjustable compositional profile and structure
- Established methodology that is capable to forming and determining the nanosegregated Pt-skin surfaces for a different class 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, thin metal films 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 MSTF, 10-fold for core/shell NPs and 7-fold for NWs.
  Mass activities improvements vs. Pt/C are 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 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, NWs and mesostructured thin films
- MSTF is the first practical catalyst with single crystalline ORR activity

Future Work

FY 2013

- Final tailoring of the compositional properties that are controlling catalytic activity of Pt-alloy systems
- Synthesis and characterization of nanosegregated Pt-alloy surfaces with higher content of TM
- Optimization of the nanosegregated catalyst of choice
- Optimization of nanosegregated mesostructured thin film catalysts with tailored structure
- Electrochemical evaluation in RDE and MEA (ANL, 3M)
- Scaling up of solvo-thermal approach to produce larger quantities of the catalysts

FY 2014

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

Collaborations

SUB-CONTRACTORS

- **Oak Ridge National Laboratory** – HRTEM
- **Jet Propulsion Laboratory** – Alloying and Combinatorial Approach
- **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