Improving stability and activity of Pt monolayer and non-Pt core-shell electrocatalysts

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Brookhaven National Laboratory

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Outline

1. Nitride-stabilized cores for improved activity / stability, and reduced Pt content in core-shell catalysts

2. Ordered non-Pt intermetallic compounds as cores and catalysts

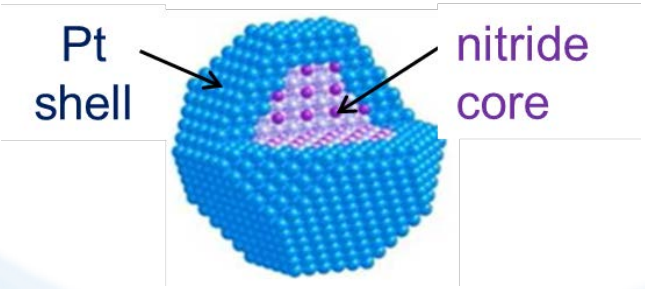
3. Ordered core-shell Pt/Ru interface for improved catalysts

4. Doped Graphene and graphene oxide – promising supports

1. Nitride-stabilized Pt-M catalysts

Pt alloys with Co, Ni, and Fe are more active for the ORR than pure Pt. Stability and Pt contents (Pt_3M) are issues.

Nitriding Fe, Co, Ni to address both issues



PtNiN/C
PtFeN/C
PtCoN/C

Nitride-Stabilized Pt-Ni Core-Shell Catalysts

Synthesis:

K_2PtCl_4 + $Ni(HCO_2)2H_2O$ + Vulcan XC72R

↓ NH_3, 500°C

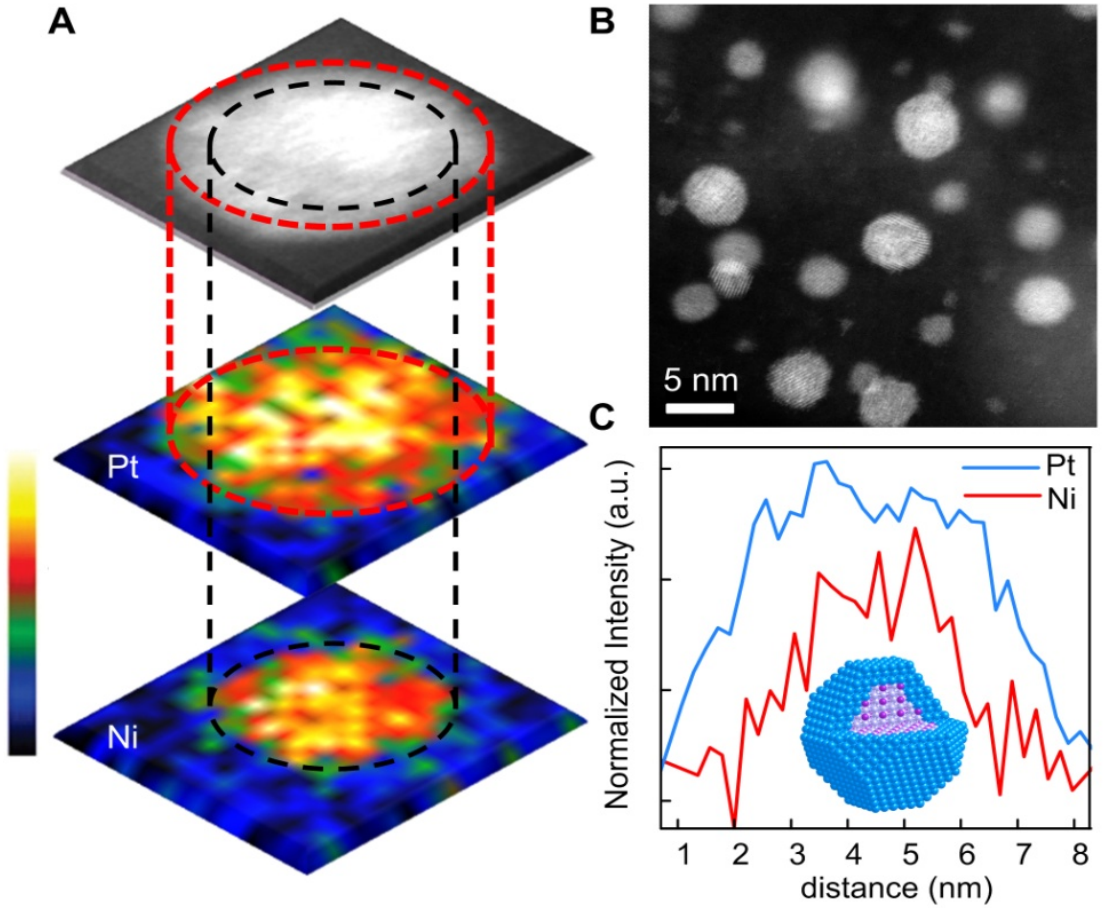
$PtNiN_x$ nanoparticles

Pt:Ni mole ratio = 1:1 (ICP)

Pt shell thickness: 0.5 ~1 nm
2 ~ 4 MLs

Average diameter: 3.5 nm

HAADF-STEM/EELS of PtNiN nanoparticles

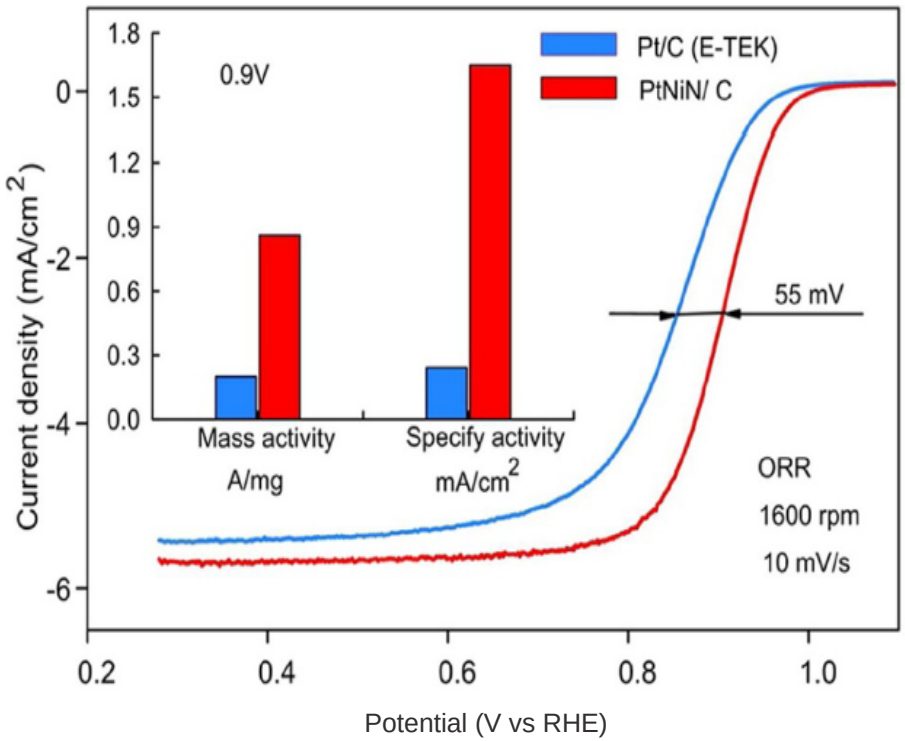


(with D. Su, BNL/CFN)

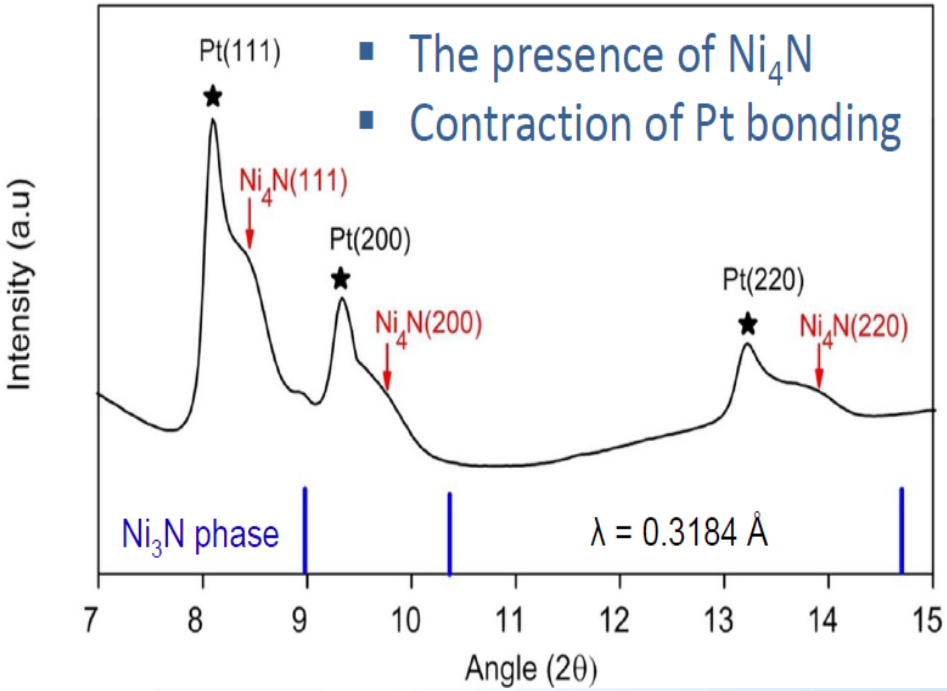
Kuttiyiel, Sasaki, Adzic, et al., *Nano Lett.*, 2012, 12, 6266
Patent: BSA 13-25

Pt on Ni Nitride Core-Shell Catalysts

- RDE - High activity of ORR



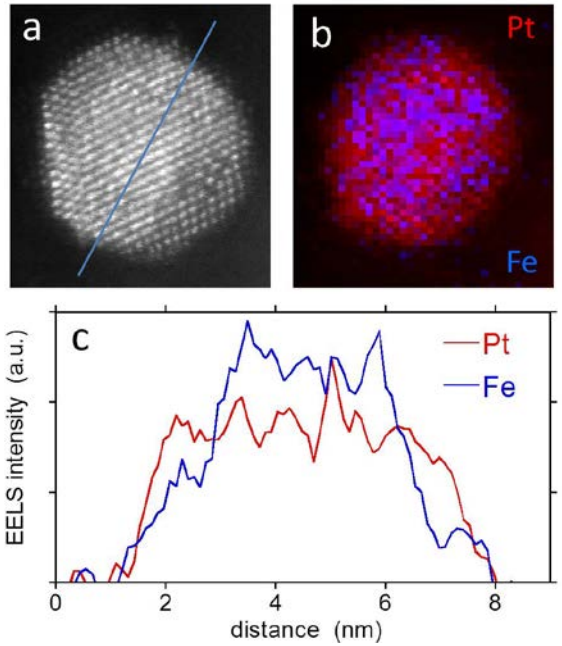
- Synchrotron XRD patterns



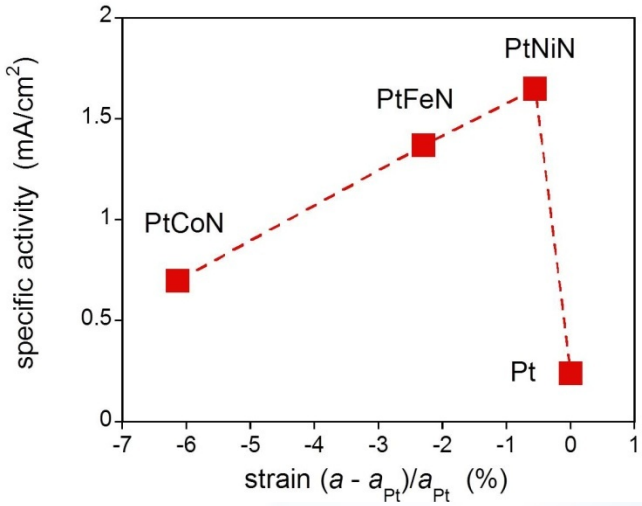
	Specific activity ($mA\ cm^{-2}$)	Mass activity ($A\ mg^{-1}$)
PtNiN/C	1.64	0.86
Pt/C	0.24	0.20

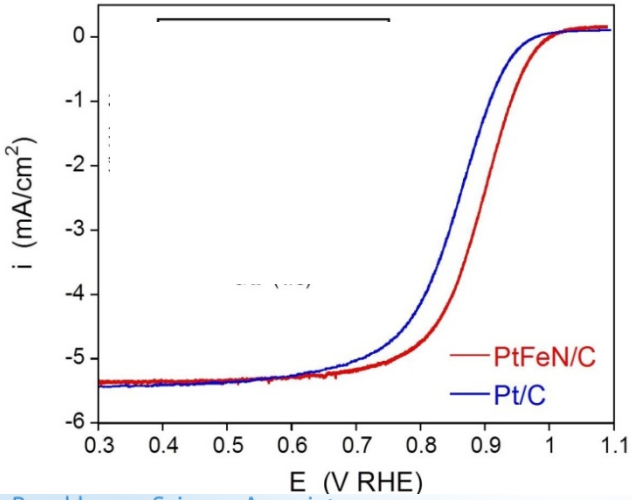
Kuttiyiel, Sasaki, Adzic, et al., *Nano Lett.*, 2012, 12, 6266;
Patent: BSA 13-25

Pt on Fe Nitride Core-Shell Catalysts

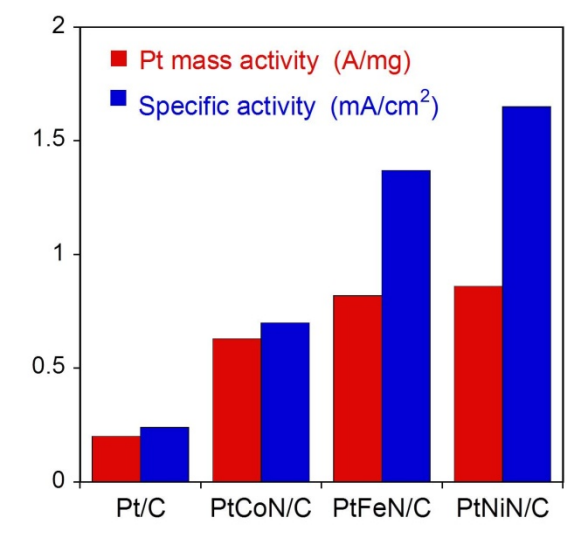


a. **HAADF image of PtFeN**
b. **EELS mapping Fe(blue) and (Pt red)**
c. **EELS line scan profiles Pt; Fe**

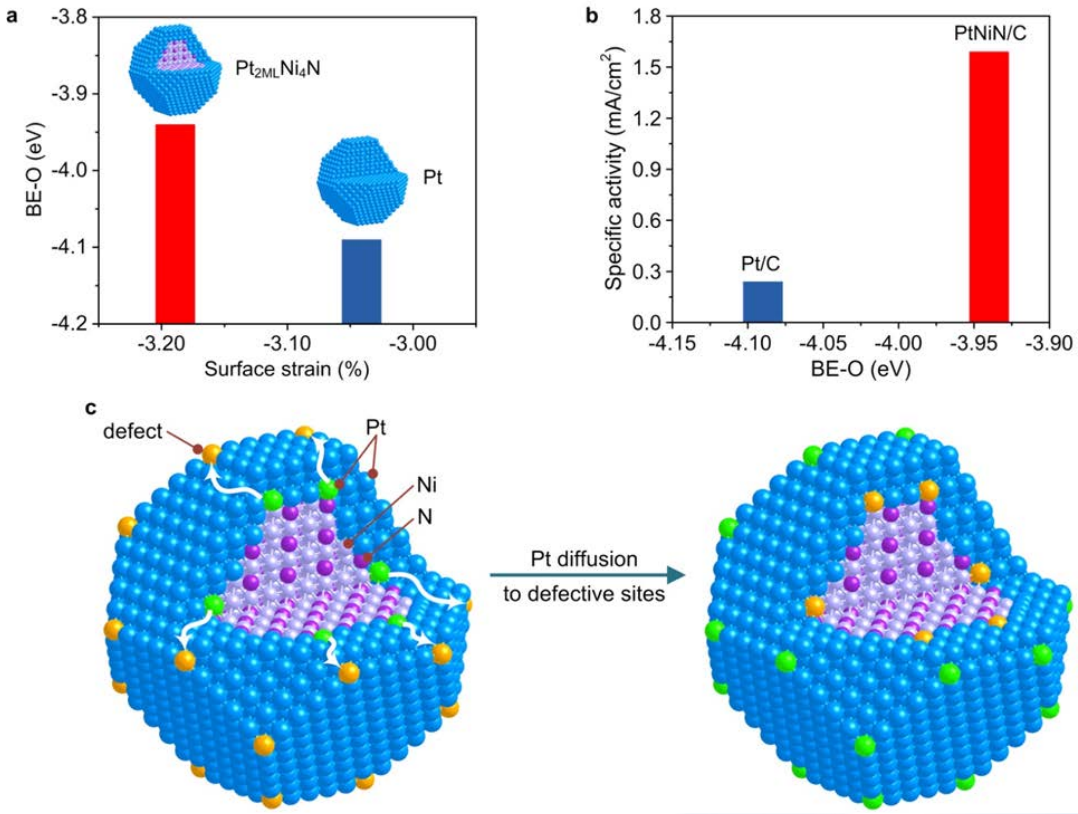




No loss in activity in 10K cycles



The role of nitriding of the Ni core for promoting NiN@Pt/C

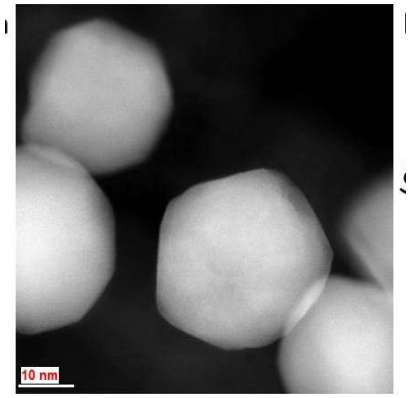


Activity : Tuning the electronic structure of the Pt shell.

Stability : Diffusion of Pt from inner shells to the surface filling the vacancy sites.

K. A. Kuttiyiel, K. Sasaki, Y. Choi, D. Su, P. Liu, R. R. Adzic, *Nano Letters* 12 (2012) 6266-6271.

2. Ordered intermetallics as non-Pt catalysts in acid media



Ordered intermetallic AuPdCo

PdCo,PdAu intermetallics as support for Pt monolayer
Ghosh et al. J. Am. Chem. Soc., 2009

AuPdCo: Non-Pt Catalysts in Acid and Alkaline Media

Synthesis:

Co salt + Vulcan carbon

↓

Add $NaBH_4$

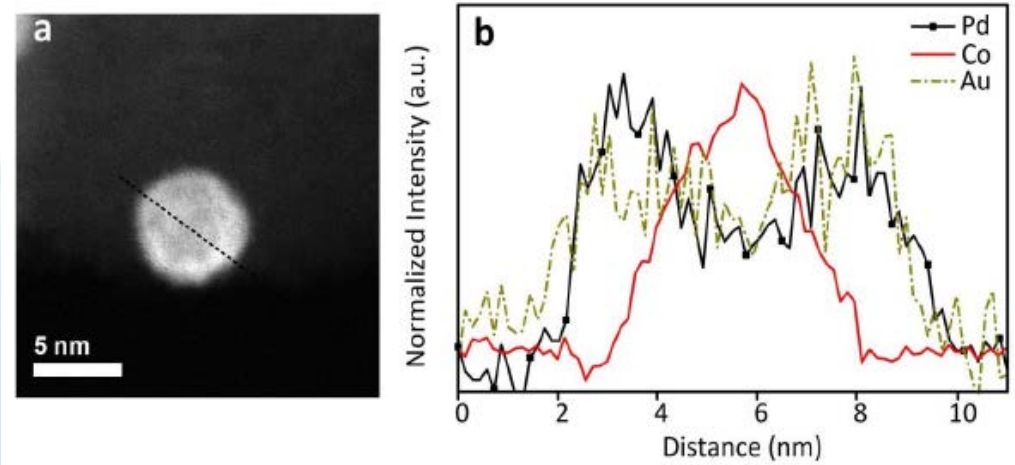
↓

Add Pd and Au salt mixture

- Ordering makes AuPdCo comparable in activity to Pt in acid/alkaline media
- Better stability than Pt in alkaline

(Au:Pd:Co = 1:4:5)

Core-shell - AuPd shell & Co core



anneal at 800°C

ordered intermetallic

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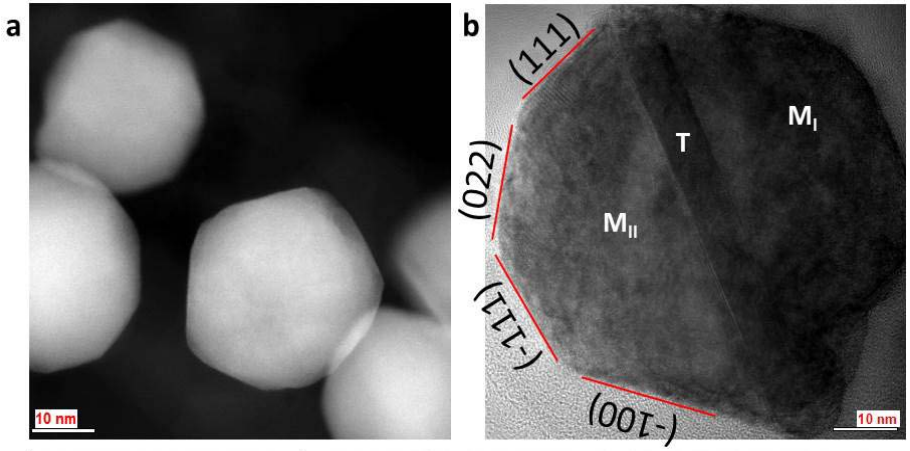
Au–Promoted Formation of Structurally Ordered Intermetallic PdCo Nanoparticles

Kuttiyiel et al., Nat. Comm., DOI:10.1038

$Au_{10}Pd_{40}Co_{50}$ catalyst

Nanoparticles are mainly spherical shaped with twin boundaries and multiple facets, with average dia 6.7 nm



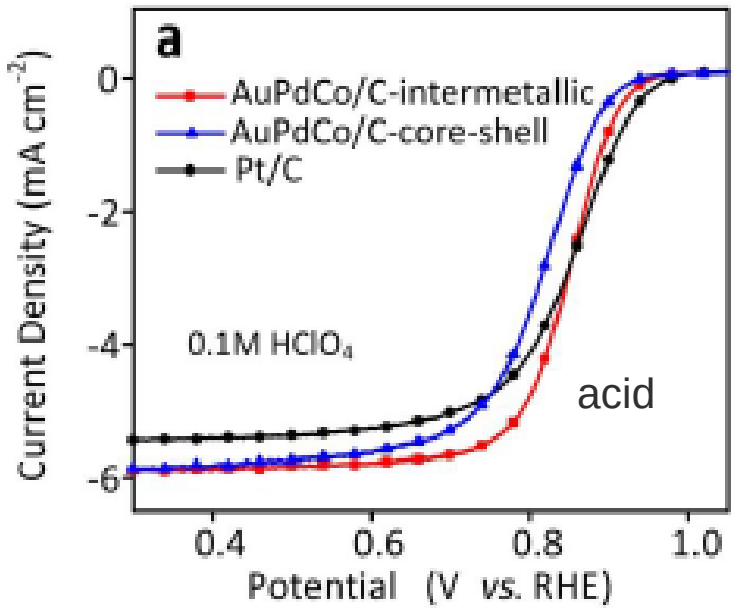
Upon addition of Au, PdCo forms a rare ordered structure with twin boundaries with stable {111}, {110}, {100} facets

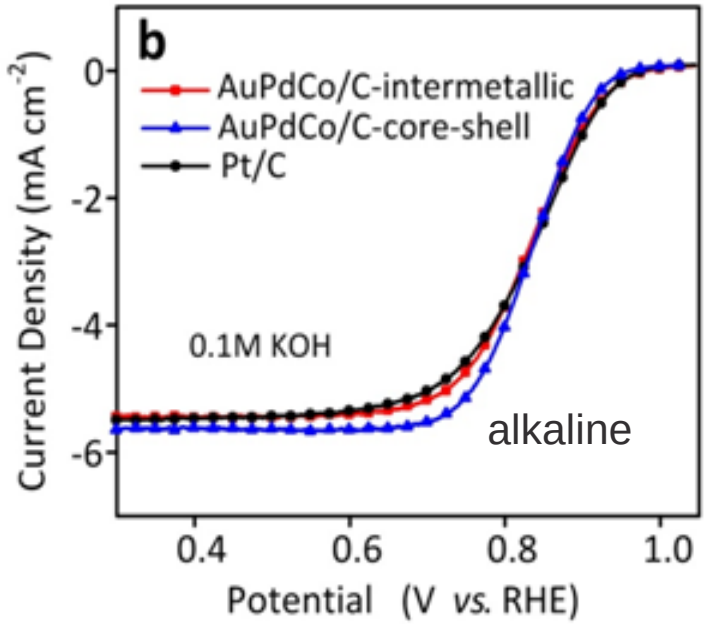
STEM and HRTEM images shows clearly twin boundaries and smooth multiple facets of AuPdCo-intermetallic nanoparticles

(**with L. Wu & Y. Zhu, BNL**)

Ordered Intermetallic AuPdCo Catalyst

❖ Promising non-Pt catalyst

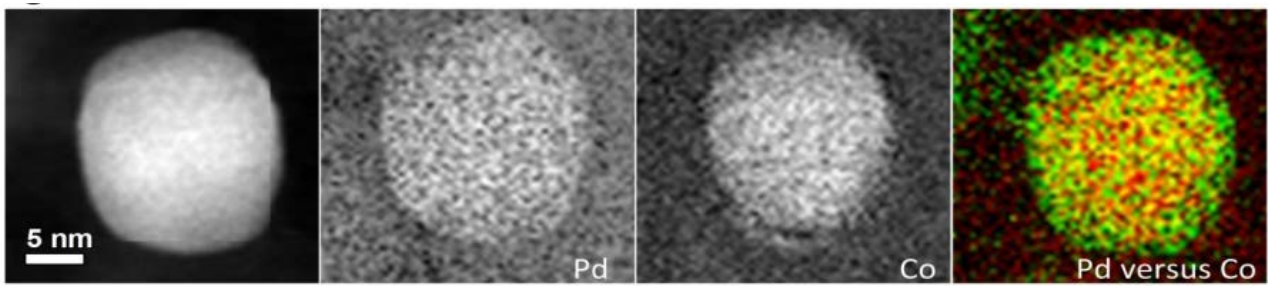




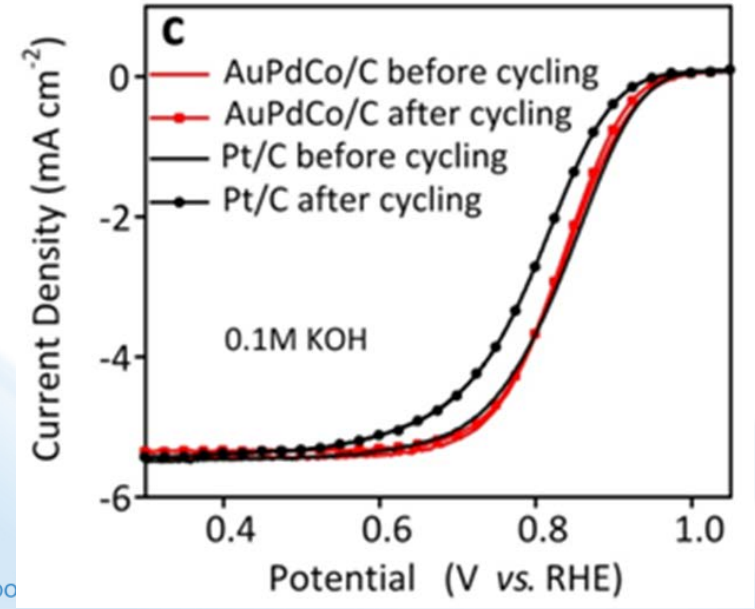
The ORR activity of ordered intermetallic AuPdCo is comparable to Pt/C in acid and alkaline solutions.

AuPdCo: Non-Pt Catalysts in Acid and Alkaline Media

Precious metal loading was **7.65 μg cm^{-2}** for AuPdCo catalysts and **6.0 μg cm^{-2} for Pt** catalyst.



EELS mapping and overlapped mapping (Pd (green) and Co (red)) showing the intermetallic structure of PdCo atoms after potential cycling

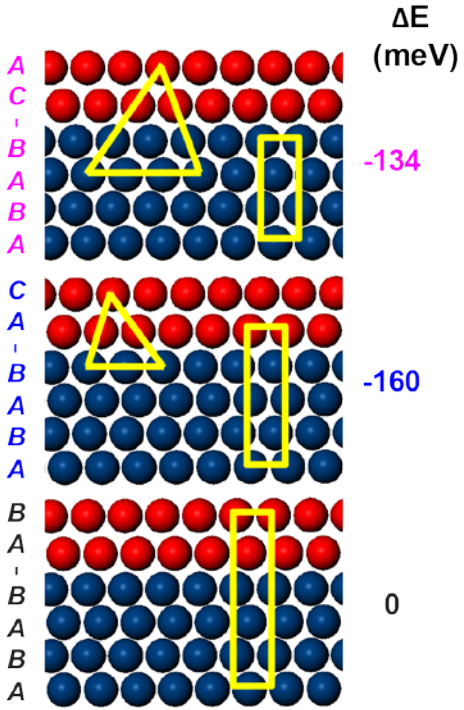


10,000 potential cycles 0.6-1.0 V

The superior stability is attributed to the atomic structural order of PdCo nanoparticles along with protective clusters of Au atoms on the surface.

3. Atomically ordered, Pt/Ru core-shell interface for enhancing catalysts' activity and durability

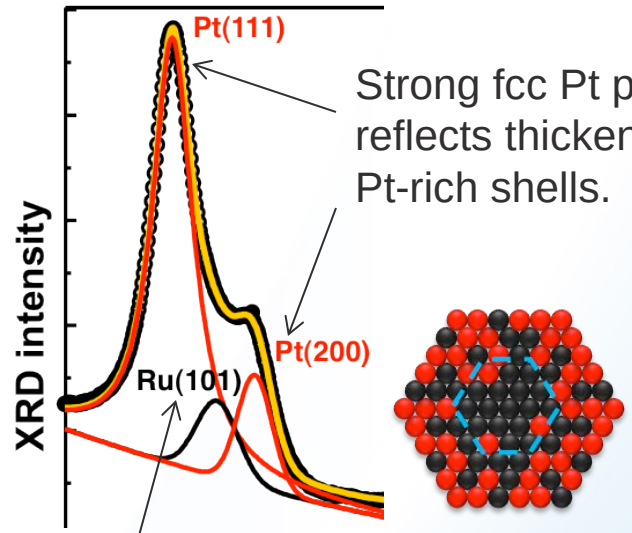
Atomically ordered Pt/Ru core-shell interface synthesized in ethanol at 80C



3D crystal structures

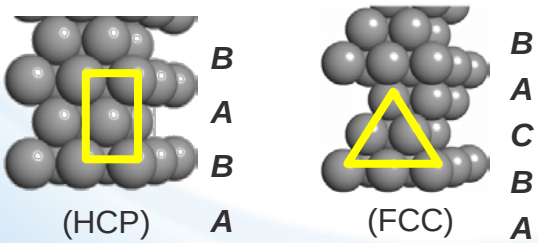
DFT shows that ordered hcp-fcc structural transition is energetically favorable for Pt bilayer on Ru.

Two favorable stacking sequence in the Pt bilayer identified: AC or CA, no B.



Strong fcc Pt peak reflects thickened Pt-rich shells.

Weak hcp Ru peak with 1.3% lattice expansion due to 22% Pt in the Ru-rich cores.



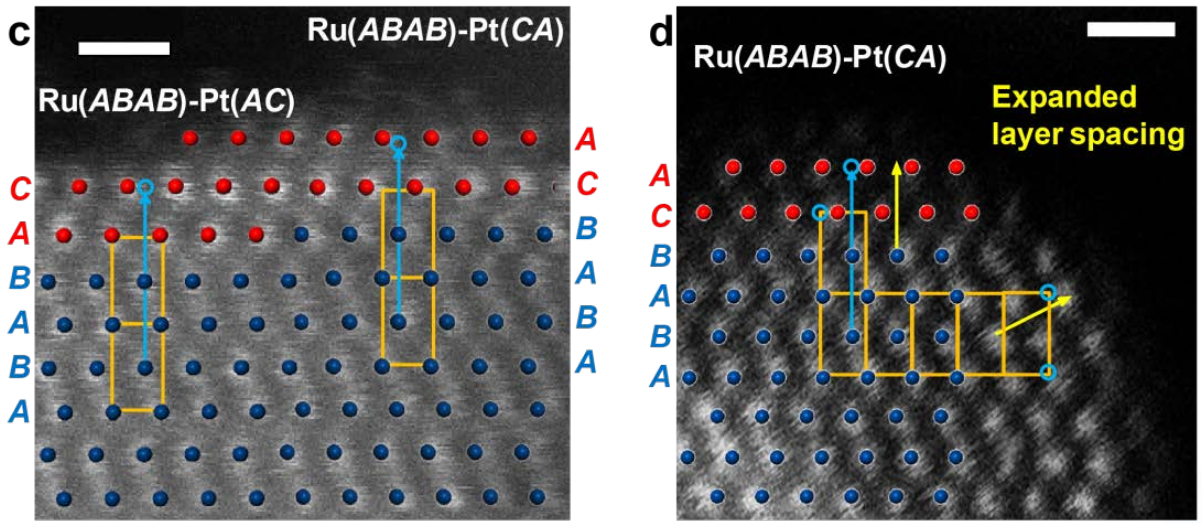
(HCP) Hexagonal Close-Packed *AB-AB-AB...*

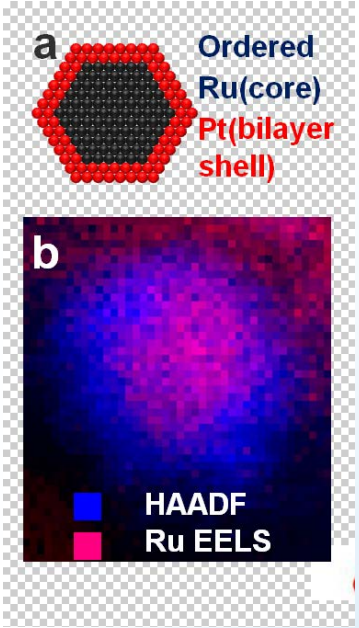
(FCC) Face-Centered Cubic *ABC-ABC*

Ru-Pt inter-diffusion causes structural disordering - partial alloy. Not for annealed Ru

Hsieh, et al., et al., Nat. Comm., DOI:10.1038,2046

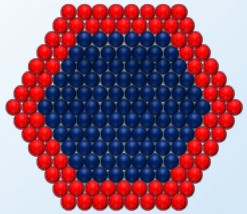
Ordered Ru-Pt core-shell interface observed by STEM





Superimposed DFT-optimized Ru-Pt interfaces (blue-red dots) match well with observed STEM images (white dots).

Ordering: switch from hcp to fcc structure

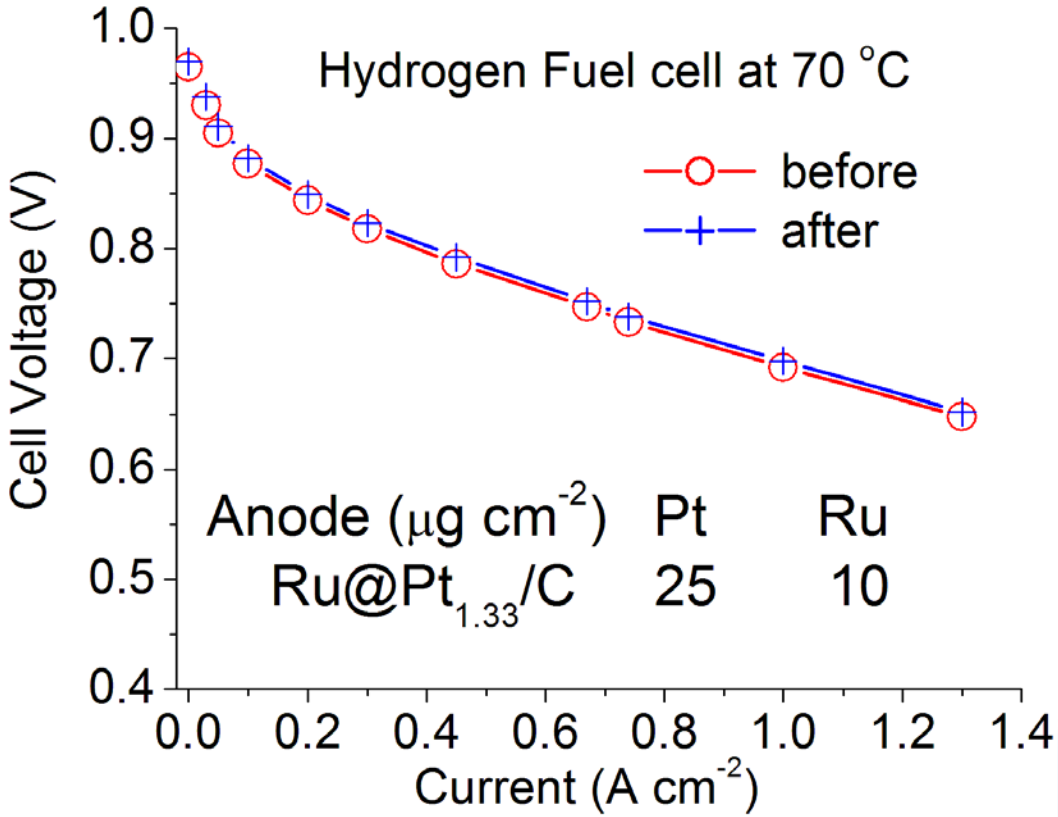


Pt (red dots) atoms shift from the hcp lattice sites (blue circles) . The yellow arrows show lattice expansion at the edges

Z-contrast intensity profiles also support a Pt bilayer shell.

Y. Hsieh et al., Nat. Commun. 4:2466, 2013

Catalytic Performance of Ordered Ru@Pt



Excellent durability

No change after 2500 cycles between 0.02 and 0.95 V over 65 hrs with only 0.025 mg cm^{-2} Pt.

Structural perfection is important

Ordered Pt bilayer protects Ru from dissolution

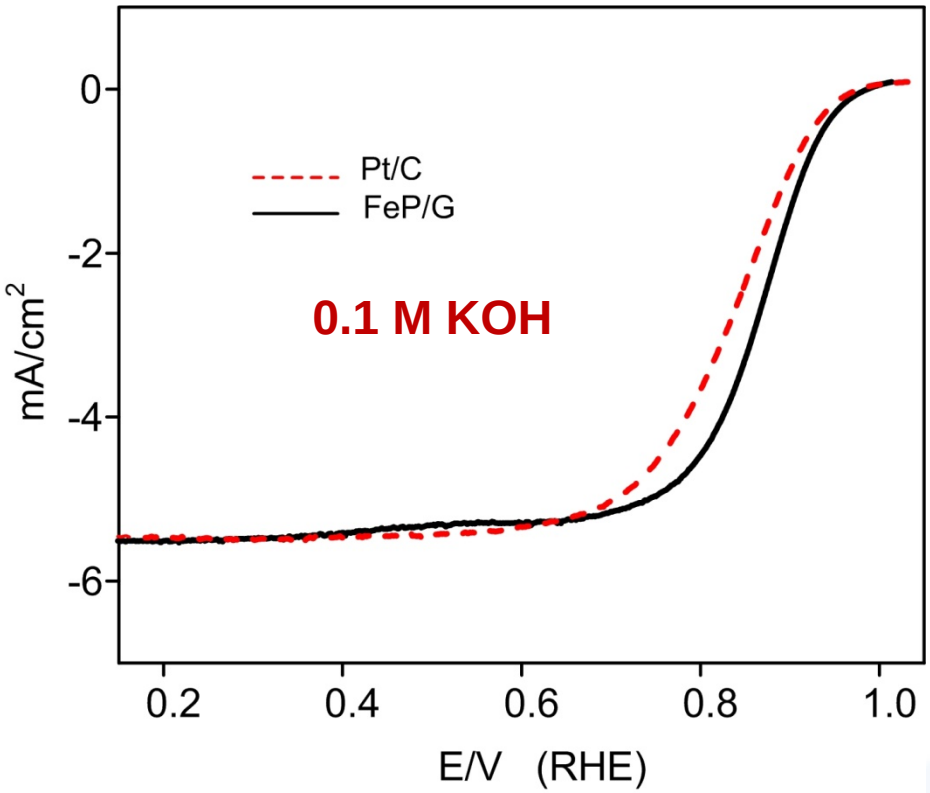
4. Graphene as support

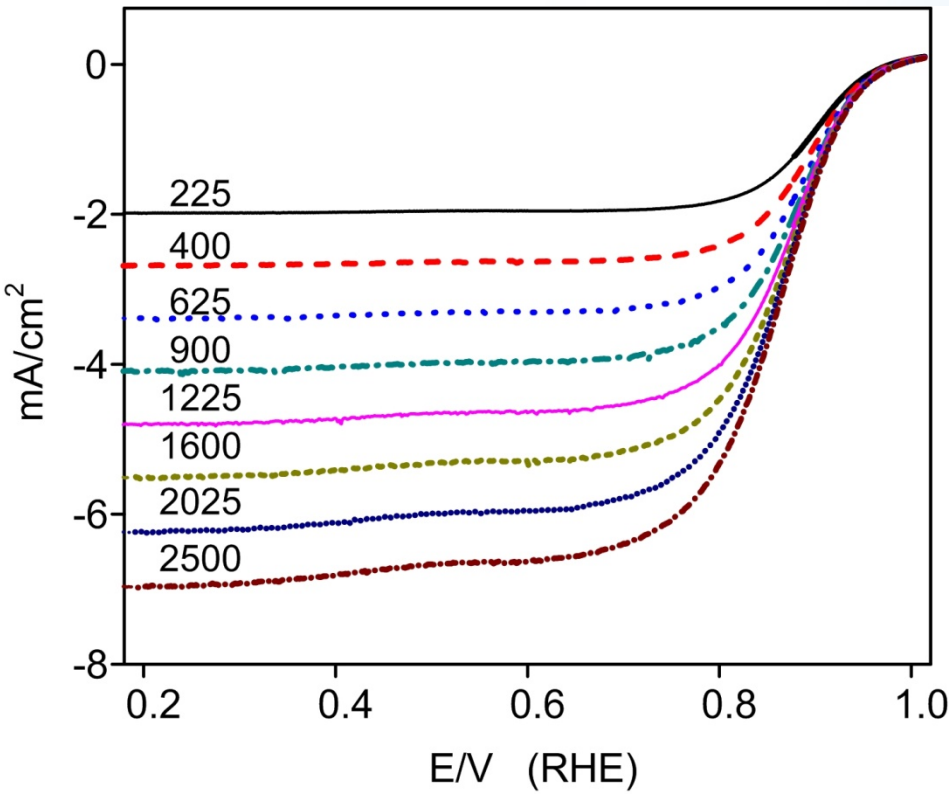
Motivation: Electronic properties easily modified by dopants
To explore new supports G-M and GN-M for Pt ML

Atomic level control of metal deposition using C*ation adsorption/reduction, adatom displacement (CARAD)* method

- Thermal treatment of Fe-porphyrin on graphene
- Potential pulse deposition of Pt on Fe/GO
- Pt deposition on GO using *CARAD* method
- Pd deposition on GO using *CARAD* method, followed by Pt ML deposition using displacement of Cu UPD on Pd.

ORR on Fe Porphyrine on Graphene treated in Ammonia at 900ºC



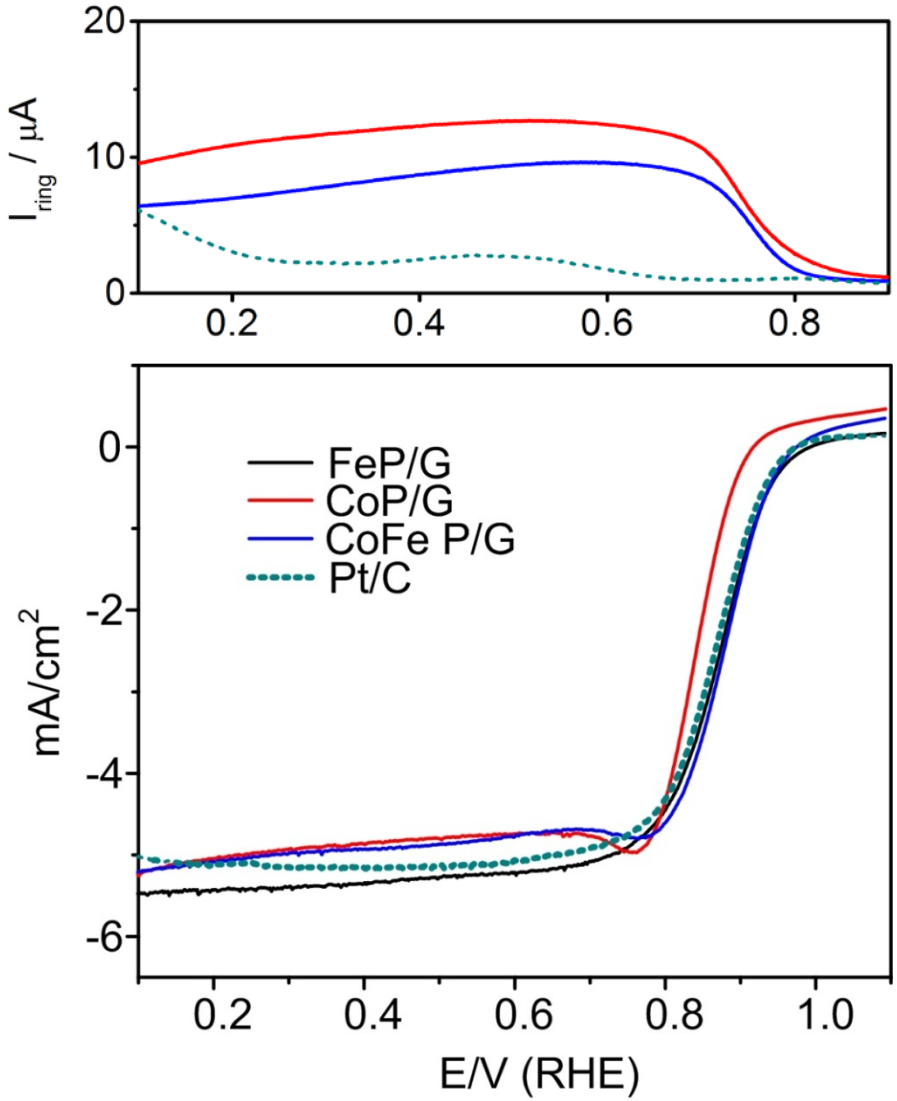


Pt loading: 6.0 ug/cm²
FeP + graphene loading: 0.4 mg/cm²

Half-wave potentials @1600 rpm
ETEK Pt/C : 840mV
Fe P/G : 868 mV

ORR on Metal Porphyrines on Graphene

0.1 M KOH



Ring Current at 1600rpm

ORR at 1600rpm

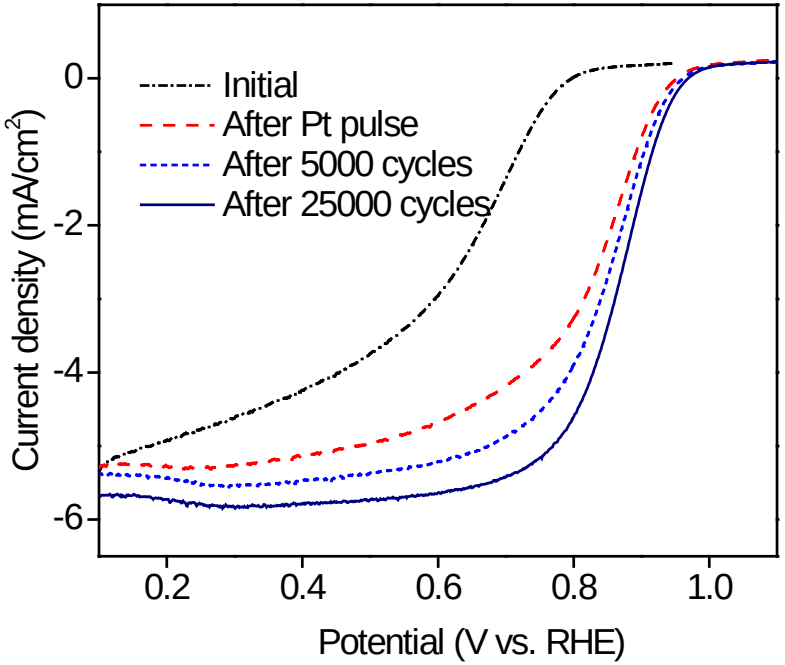
ORR on Metal Porphyrines on Graphene in 0.1 M KOH

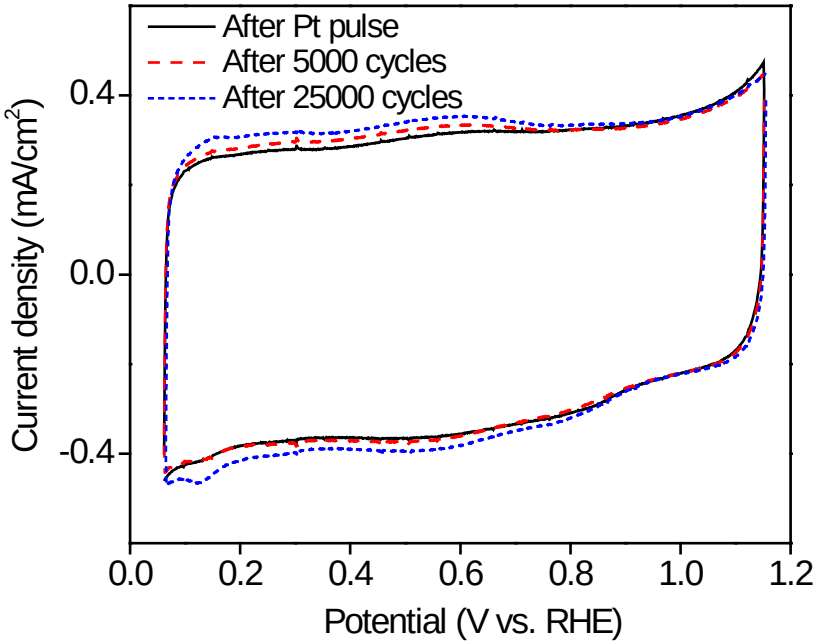
Catalyst / (loading)	Onset Potential (V)	Half Wave Potential (mV)	Half Wave Potential after **5000 cycles** (mV)
CoFeP/G ($0.4 mg/cm^2$)	0.97	880	867
CoP/G ($0.4 mg/cm^2$)	0.92	845	840
FeP/G ($0.4 mg/cm^2$)	0.99	870	860
Pt/C ($0.1 mg/cm^2$) Pt: $10.2 ug/cm^2$	0.97	868	838

Electrolyte: 0.1 M KOH; Scan rate: 10mV/s ; Cycling: 0.65 – 1.0 V in air

ORR on Pt on Fe Porphyrine on Graphene

Pt pulse deposition on 5% FeP supported on Graphene annealed at 700° C in NH_3





Half wave potentials (mV)		A/mg_{Pt}
Initial	633	
After Pt pulse	838	0.69
After 5000 cycles	853	0.73
After 25000 cycles	869	0.85

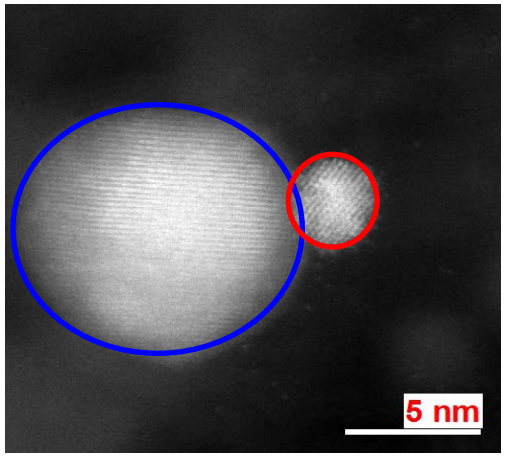
RDE loading 0.2mg/cm^2
Cycling at 50mV/s from 0.6-1.0 V in air

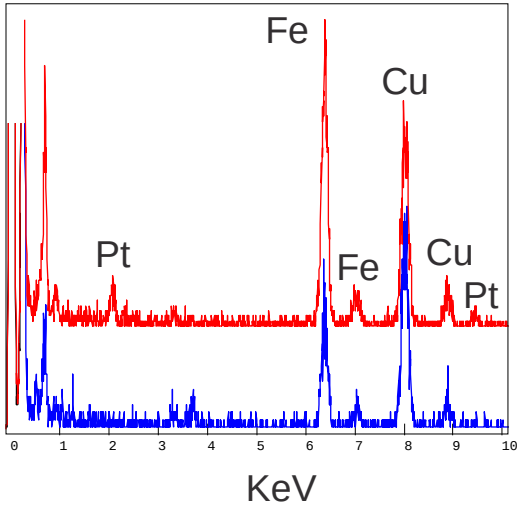
*Pt pulse deposition at 1 sec from 0.4-0.9V (RHE), then OCP for 30sec and repeated 5 times.

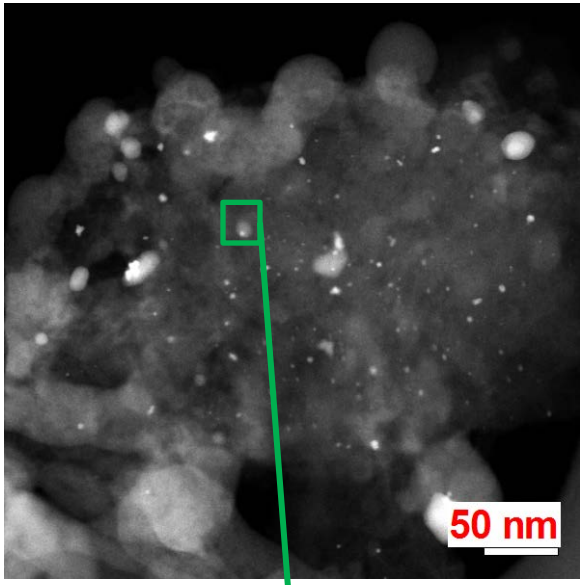
Pt loading: 2.1 μg/cm^2

Pt pulse deposition on 5% FeP on Graphene annealed at 700° C in NH_3

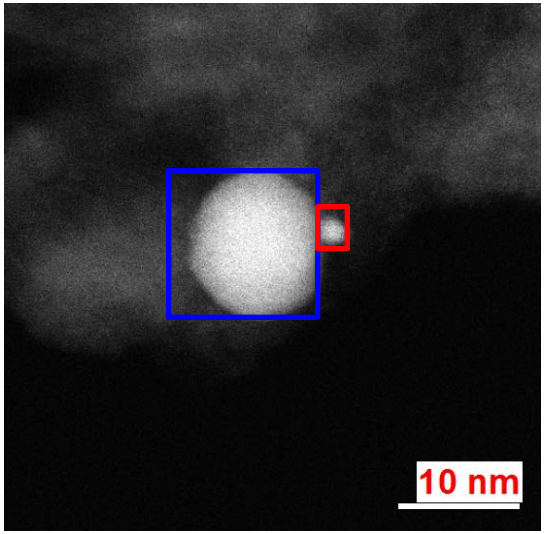
Nucleation of Pt occurs preferentially on Fe;

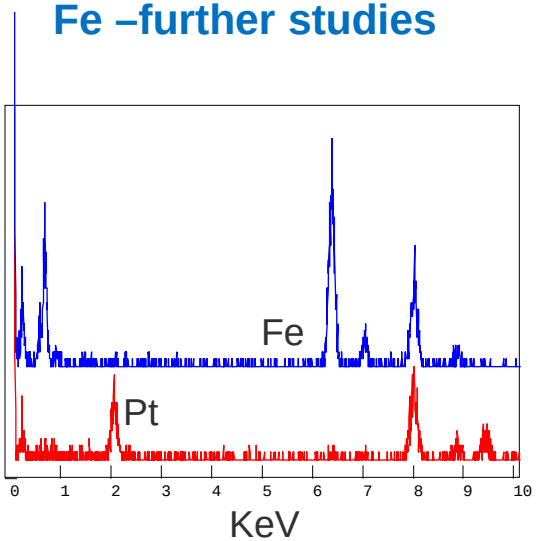


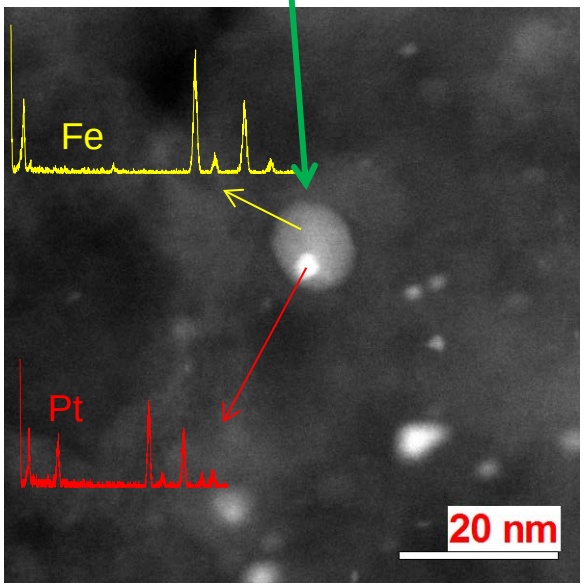




Origin of stability of Fe –further studies



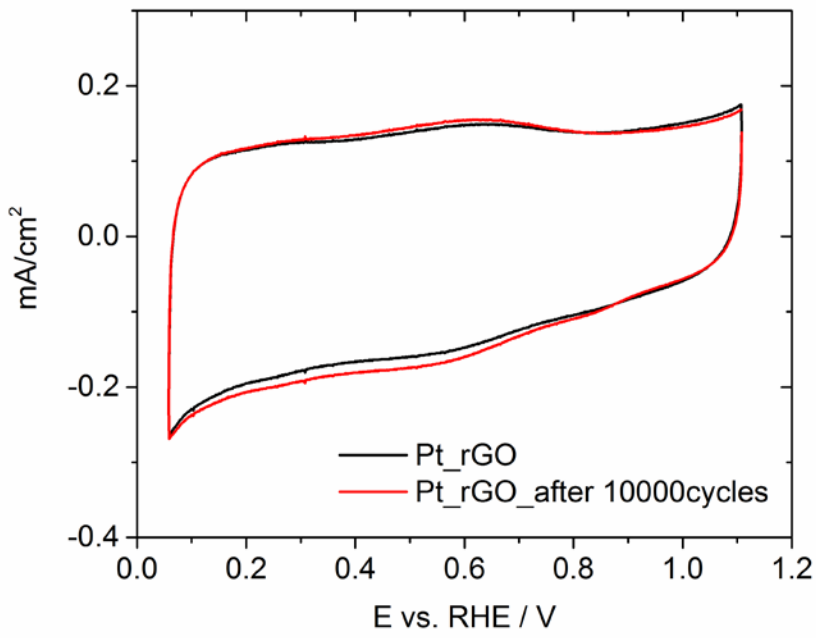


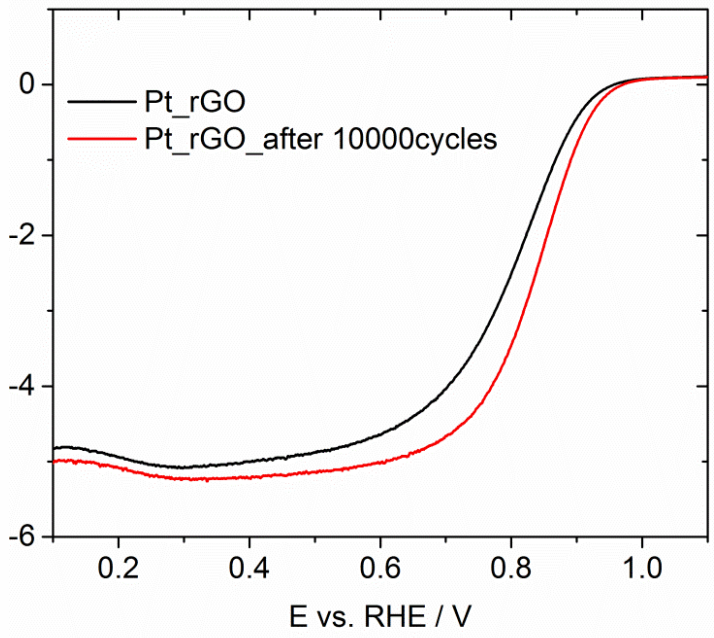


STEM-HAADF image and EDS of particles after 25000 cycles show that the large and small particles are Fe and Pt, respectively.

Pt deposited on GO

Pt deposited on Reduced Graphene oxide using CARAD method
Plumbite adsorption/reduction, Pb adatoms displaced by Pt

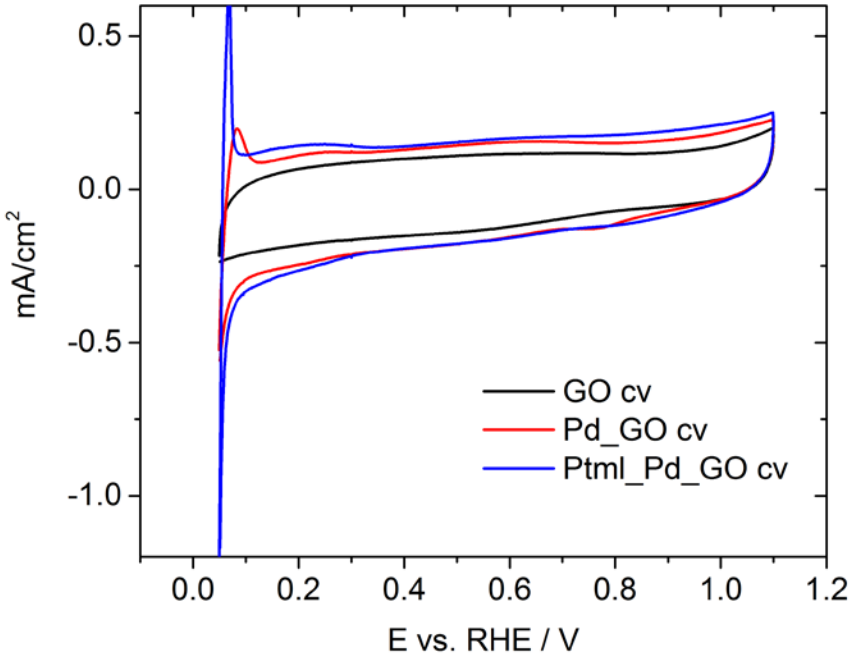


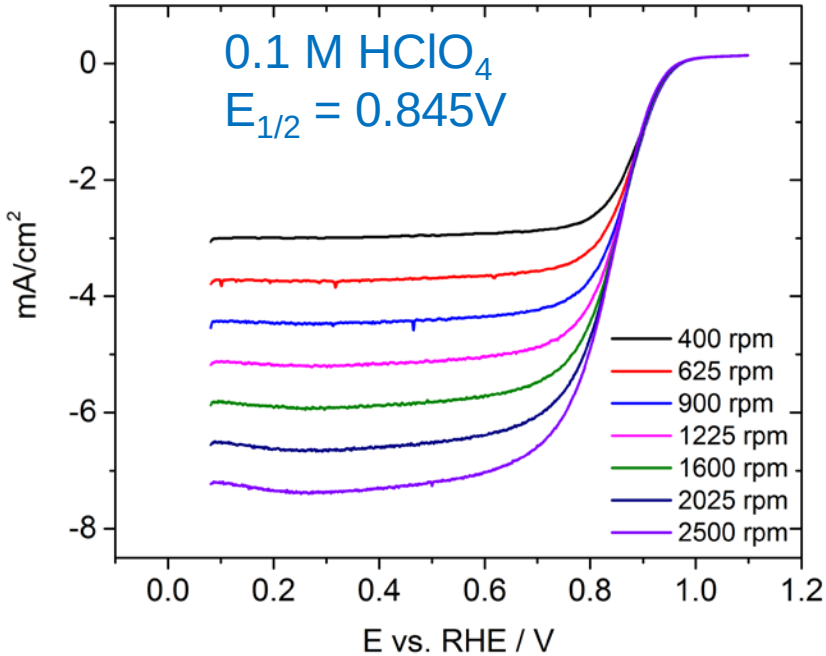


	Half Wave Potential (mV)
Initial	803
10000 Cycles (0.6 – 1.0V in air)	838

Pt ML on Pd/GO

Pd deposited on Reduced Graphene oxide using
CARAD method .
Pt monolayer deposited on Pd using Cu UPD displacement.





Total Pt: 0.51 µg/cm²

Pt Mass Activity: 2.47 A/mg

Conclusions

- Nitriting non-noble metal core constituents can increase stability, activity, while reducing noble metal shell content PtMN (M=Ni, Fe, Co) compared to Pt_3M stoichiometry.

- Ordered intermetallic compounds offer an excellent possibility for designing non- Platinum catalysts.

- Ordering the interfacial region of core-shell nanoparticles can cause profound catalysts improvements.

- Graphene as support offers numerous possibilities for designing improved catalysts.

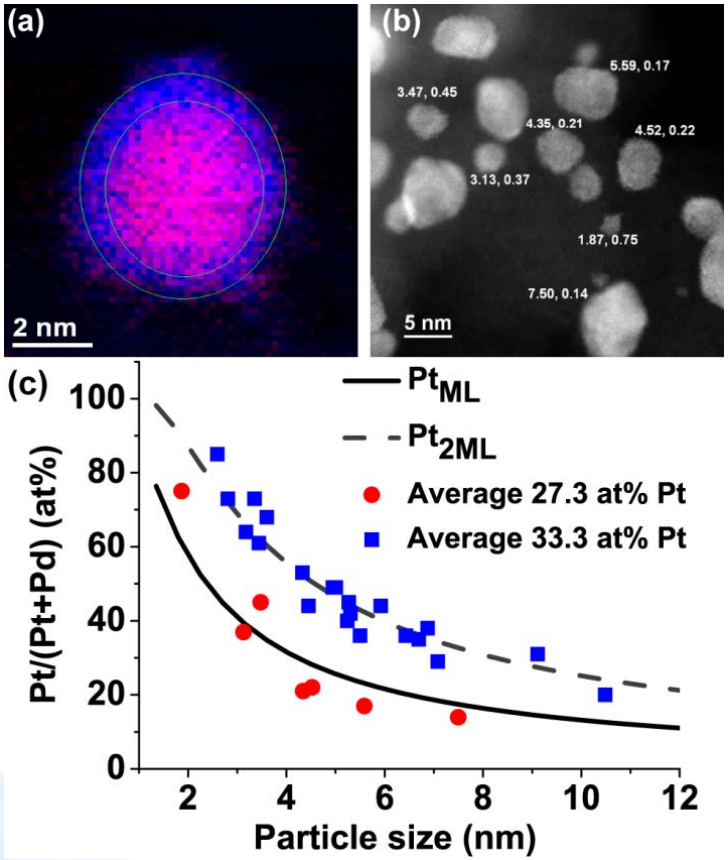
Acknowledgements

Fundings

U.S. DEPARTMENT OF ENERGY EERE

Ordering at the core-shell interface: Epitaxial Pd@Pt ML and BL

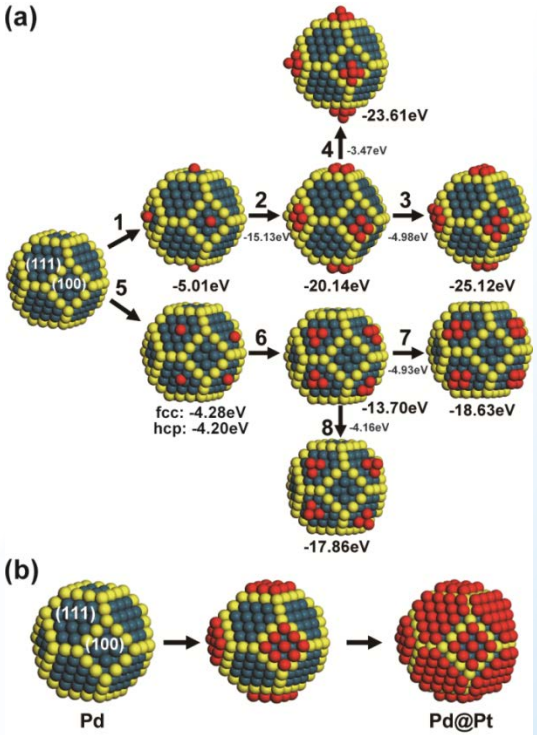
Exclusive deposition of Pt on Pd

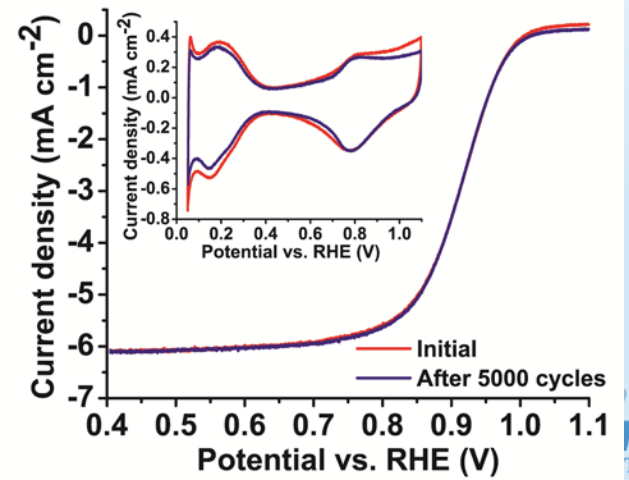


The ratio Pt/(Pt + Pd deceases for two Pt ion conc with particle size along the lines calculated for ML and BL.

Deposition Mechanism

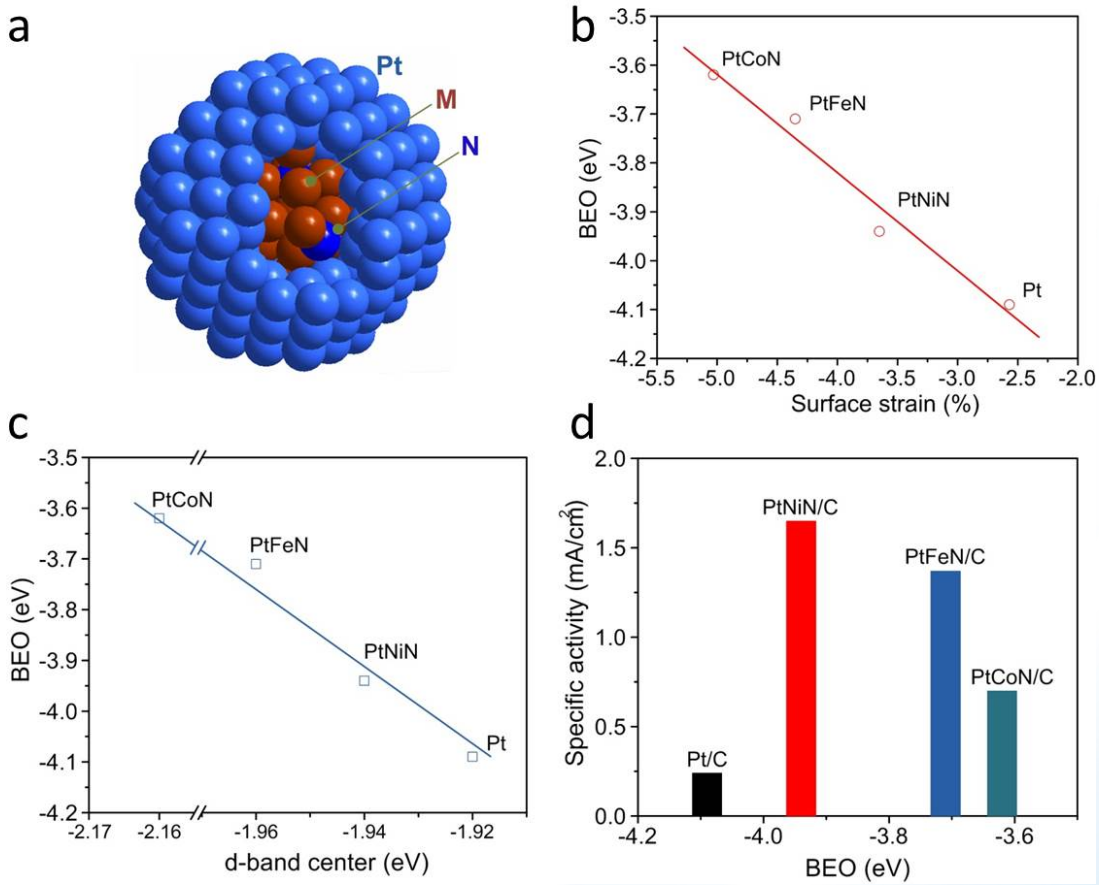
2D Pt first on Pd(100) then on Pd(111)





DFT Calculations using a Model PtM_4N (M= Ni, Fe, Co)

Calculated lattice parameters for PtM_4N are in line with the experiment
Nitride cores weaken the BEO in comparison with Pt.



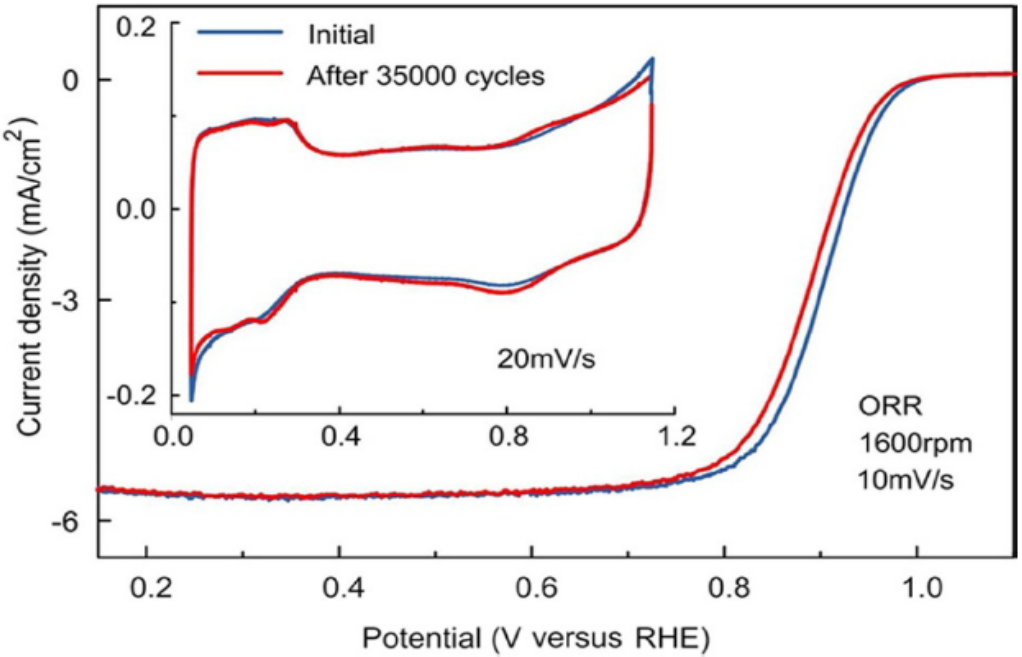
Alloys activity: PtFe > PtCo/C> PtNiC ; Nitride added: PtNiN/C > PtFeN/C > PtCoN/C

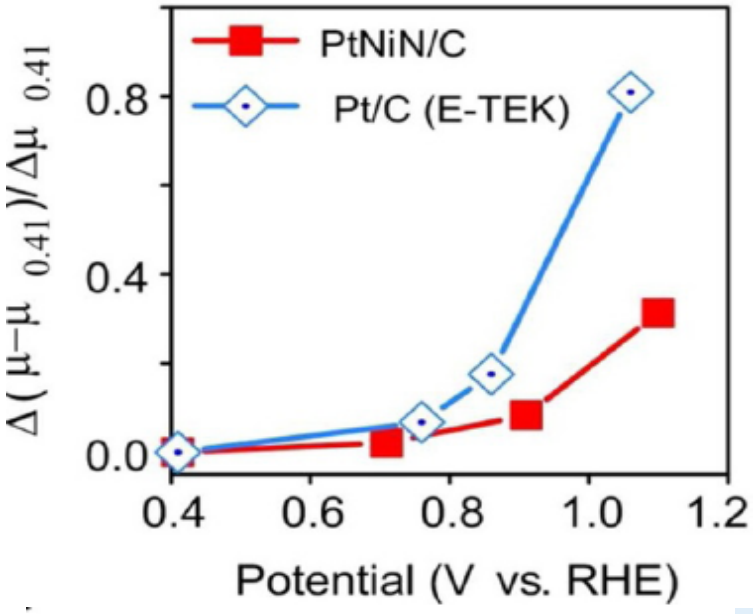
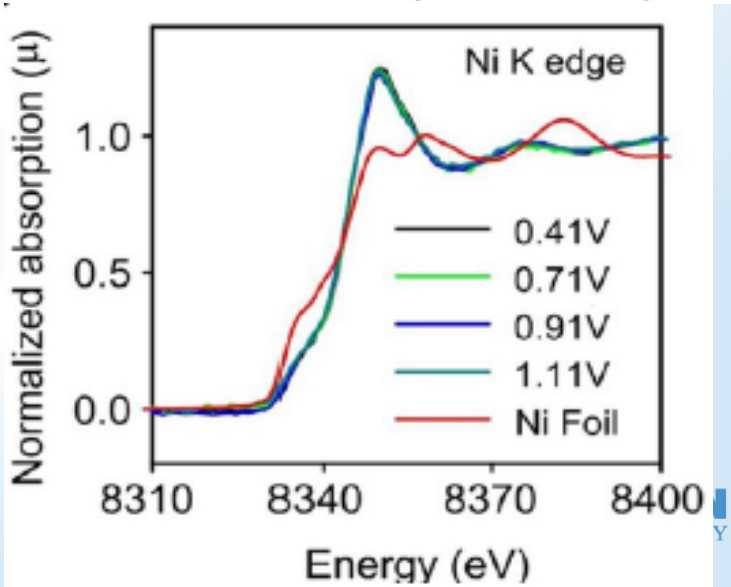
Pt bonds oxygen too strongly, while FeN and CoN cause too much strain.

Both, electronic and geometric effects are essential for increased ORR activity

Pt on Ni Nitride Core-Shell Catalysts

- High stability - little change in ECSA & small decrease in $E_{1/2}$ after 35k potential cycles



- Stable **Ni_4N** cores under elevated potentials

- Delayed oxidation of Pt