Project FC141

Platinum Monolayer Electrocatalysts

Recent Results

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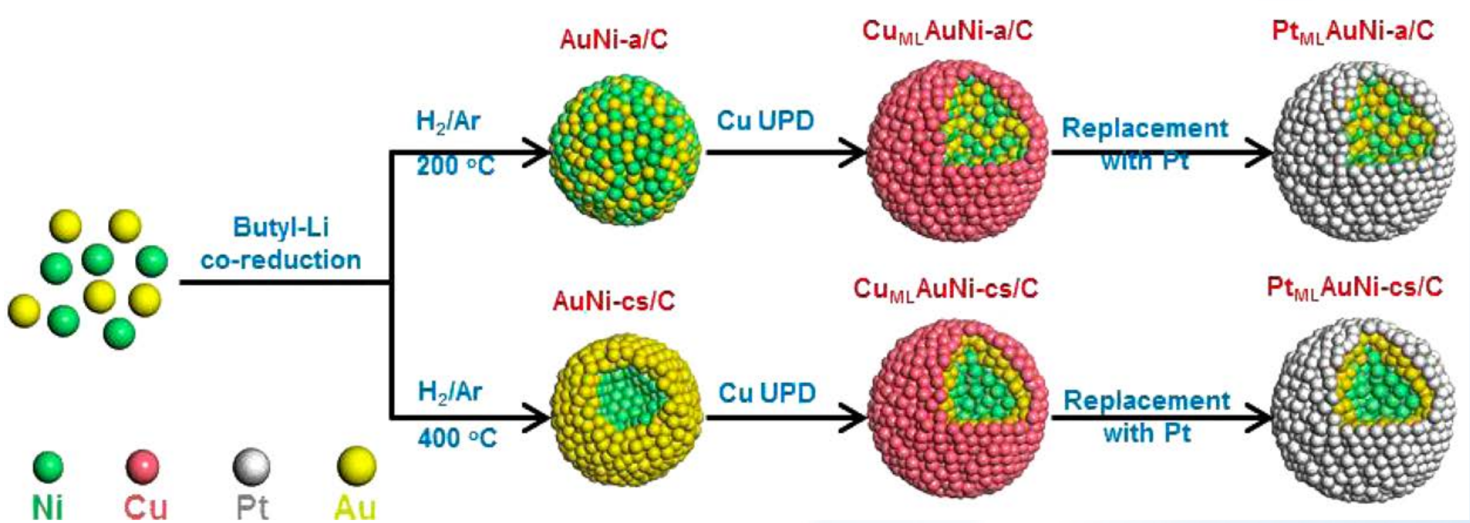
Recent results

1. Optimizing composition and structure of bi-metallic cores
2. Refractory metal cores
3. New classes of core-shell catalysts
    - 3.1. Particles with oxides segregated to edges and vertices.
    - 3.2. Electrodeposition of Y, and Y - Pt alloys from ionic liquids.
    - 3.3 Janus nanoparticle electrocatalysts

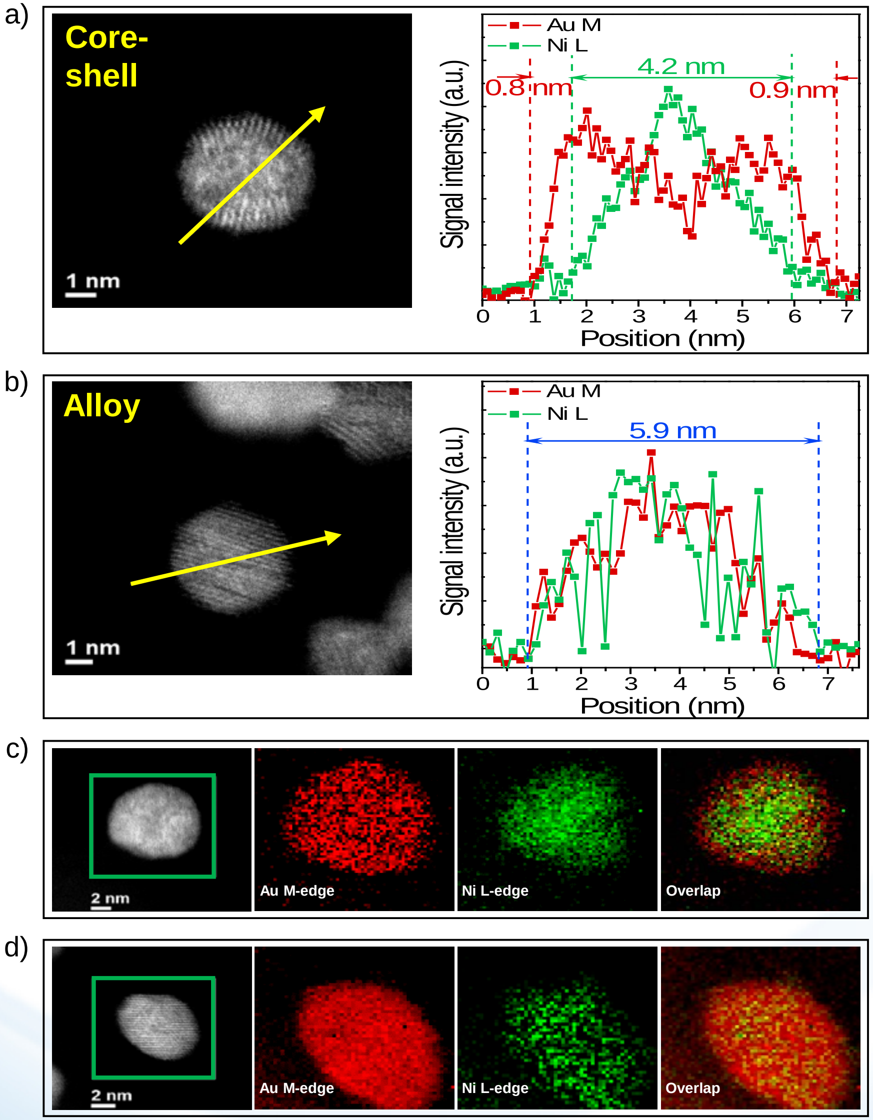
Optimizing core structure and composition: alloy vs. core-shell particles

Strong effect of the structure of bimetallic AuNi cores on the activity of Pt shell

Pt_{ML}/AuNi–cs and Pt_{ML}AuNi-a



Optimizing core structure and composition: alloy vs. core-shell particles

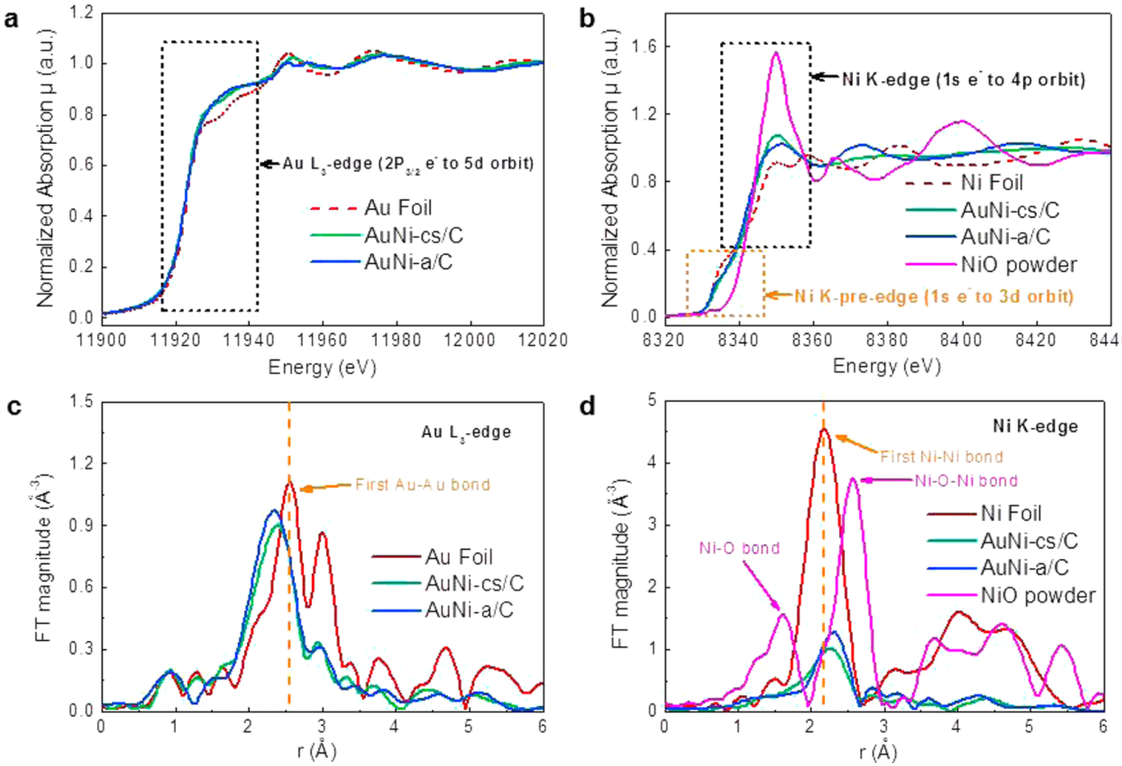


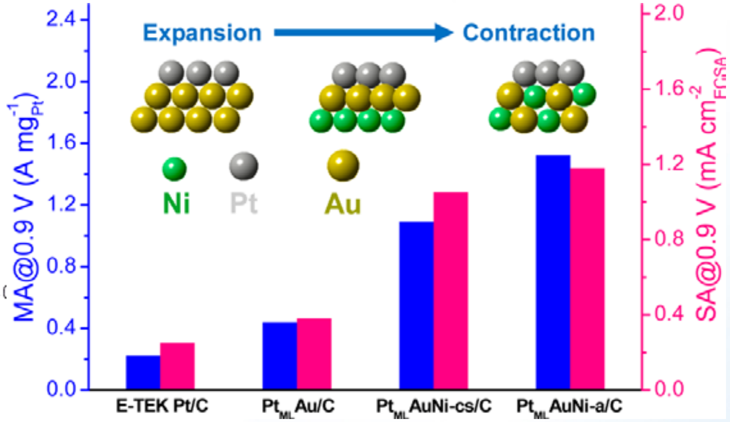
Interaction of alloyed AuNi with a Pt shell makes it more active for the ORR than that with AuNi core-shell nanoparticles.

HAADF-STEM images and EELS line-scan profiles of Au (red) and Ni (green)

Chen et al. Chem. Mat. DOI:10.1021acs.chem.mat.6b00500

Optimizing core structure and composition: alloy vs. core-shell particles





XAS studies. (a, b) XANES spectra and (c, d) FT-EXAFS spectra of Au L3 and Ni K edges obtained from AuNi-cs/C, AuNi-a/C, and the references (Au foil, Ni foil, and NiO powder).

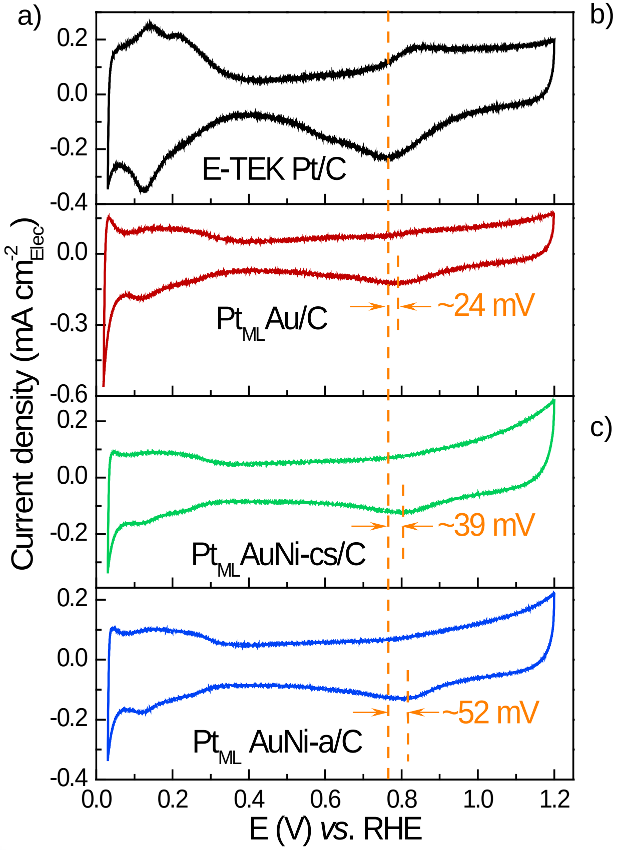
The $2p_{3/2}$ electrons to a vacant 5d-orbit, and therefore, AuNi-a/C and AuNi-cs/C had a partial depletion of the Au d-band in relation to pure Au

The larger Au-Au bond distance for core-shell - interaction of Ni atoms is much higher for the alloyed nanoparticles.

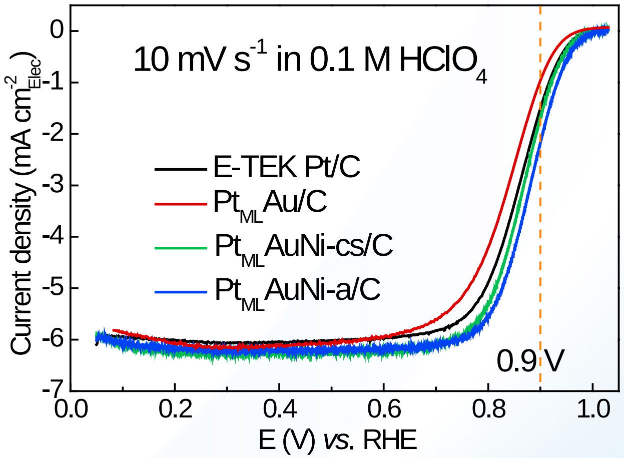
The Ni-Ni peak shifts of AuNi-a/C and AuNi-cs/C to larger lengths attributed to the geometrical effect by Au.

The lower Ni-Ni distance for the AuNi-cs/C indicates smaller Au-Ni interaction for the core-shell structure.

Optimizing core structure and composition: alloy vs. core-shell particles



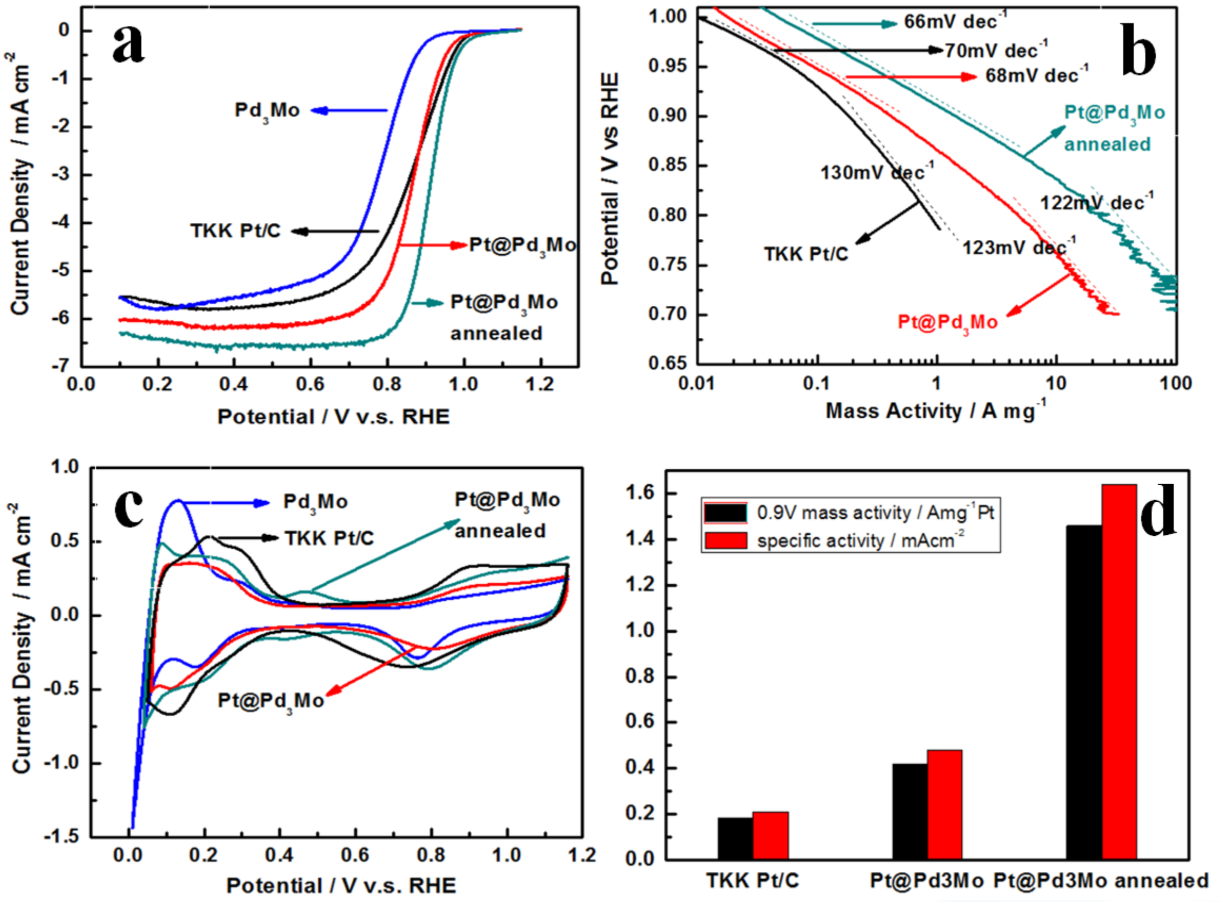
Electronic effects of the alloy change the O_2 and H_2O interaction with the Pt shell and facilitate increased ORR kinetics.

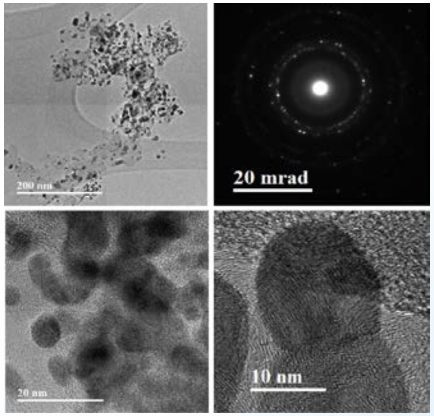


PGM Activity:
$AuNi_{alloy}$= 1.52 A mg^{-1}
$AuNi_{core\text{-}shell}$ = 1.18 mA cm^{-2}

Stability (5000 potential cycles):
$AuNi_{alloy}$: almost no loss
AuNi $_{core\text{-}shell}$: 25mV loss in $E_{1/2}$

Mo-modified cores: Pt_{ML} on Pd-Mo core

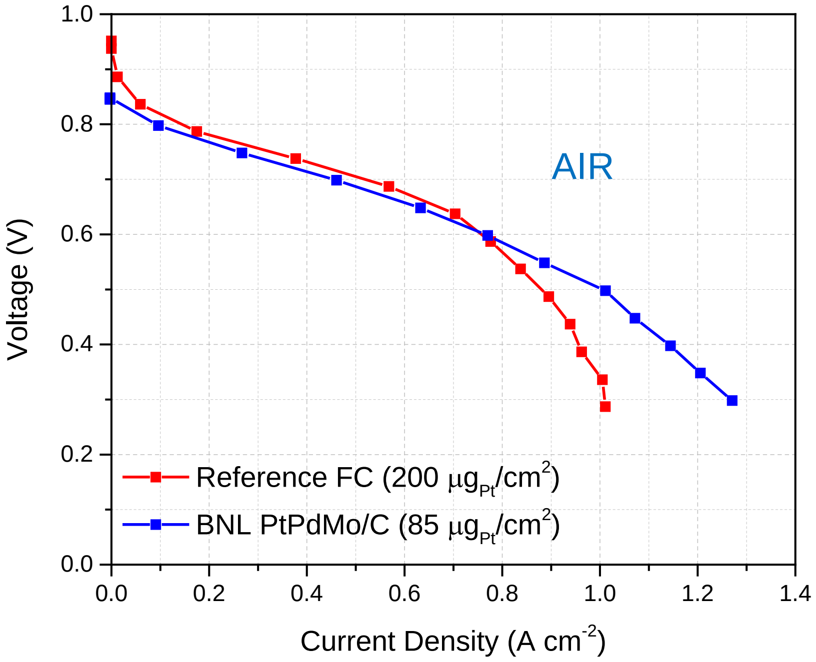


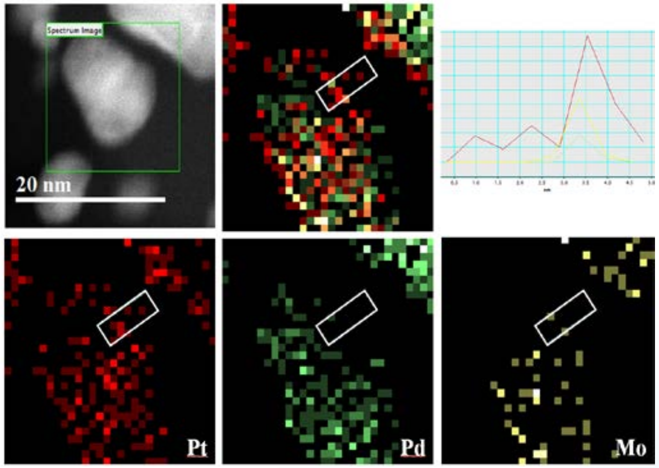


The Pt monolayer on Pd_3Mo has 7 and 8 times higher mass and specific activities than commercial catalyst.

PGM mass activity is expected to increase with improved synthesis.

Mo-modified cores: Pt_{ML} on Pd-Mo core





EDS mapping of the as prepared $Pt@Pd_3Mo/C$ catalyst

The lattice parameter for the catalyst is smaller than that of pure Pd - compressive strain

Metallic Mo instead of Mo oxide helps the ORR activity, the same with Pd.

Cathode: BNL PtPdMo/C ca. 85 $ug_{Pt}cm^{-2}$, 13 $ug_{Pd}cm^{-2}$, air, 200 sccm, 1.0 bar air;
Anode: Commercial GDE ca. 0.2 $mg_{Pt}cm^{-2}$; **Membrane**: Nafion®,211; Cell: 80°C;
Reference Fuel Cell: 0.1 mg cm^{-2} anode; 0.2 mg cm^{-2} cathode; 47 wt.% Pt/C (TKK).

Refractory metal cores: Pt monolayer on Nb@Pd cores

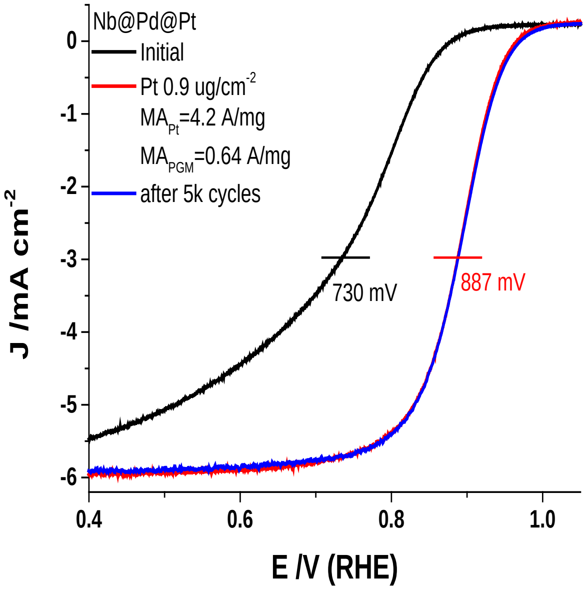
Synthesis:

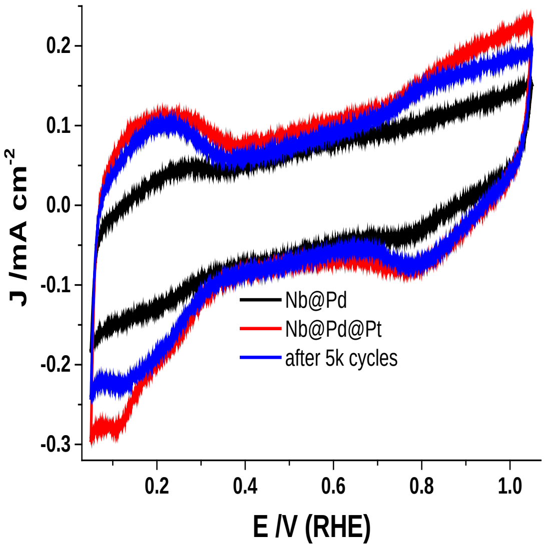
(1) Mixture of $NbCl_5$ and $PdCl_2$ with Vulcan XC-72 carbon annealed at 650℃ for 1 h in H_2 and then at 300℃ for 1h in Ar.

(2) Pt shell was deposited on Nb@Pd/C nanoparticle surfaces using the galvanic displacement of Cu layer formed by Cu underpotential deposition (UPD)

MA = 4.2 A/mg$_{Pt}$

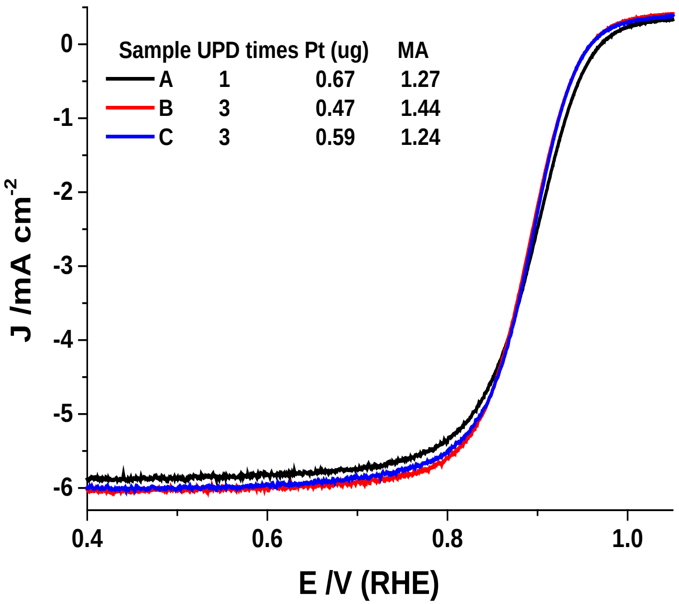
MA = 0.64A/mg$_{PGM}$





Pt/PdNb/C has a very good activity and durability

Ru@Pd@Pt double-shell ORR catalysts for enhancing cost-equivalent-Pt mass activity



Motivation:

- Lowering metal cost - The price ratio for Ru:Pd:Pt is about 1:10:20 . Improving core stability - Ru binds carbon exceptionally strong and can induce a lattice contraction of the Pd shell to stabilize Pd.

Preparation methods:

- Ru core on carbon support was synthesized from ethanol solution containing $RuCl_3$.

- Pd coating of Ru was made in ethanol solution containing Na_2PdCl_4.

- Pt shell was added via replacing Cu UPD layers.

Catalyst	Ru	Pd	Pt	MA_{Pt}	MA_{PGM}	MA_{Pt-eq}
	ug	ug	ug	A/ mg	A/ mg	A /mg
Pd@Pt A	0	3	0.67	1.25	0.23	**0.39**
Ru@Pd@Pt B	1.5	2	0.47	1.44	0.27	**0.44**
Ru@Pd@Pt C	1.5	2	0.59	1.24	0.28	**0.44**

$E_{1/2}$ (mV)	BOL	5K	10K	$dE_{1/2}$	Size (nm)
Ru@Pd@Pt	874	874	875	+1	3
Pd@Pt	900	881	886	-14	6

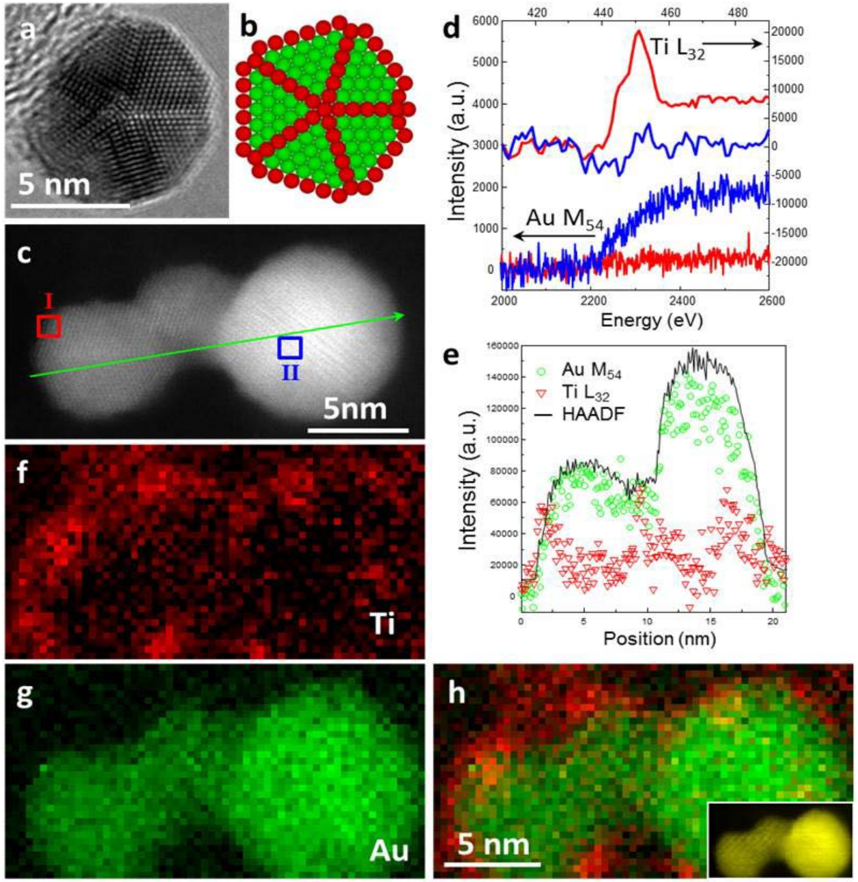
New class of core-shell catalysts

Catalysts with oxidized component preferentially segregated to edges and vertexes

Pt monolayer on TiO_x decorated Au cores

Au and Ti co-deposited by reduction of solution of their salts

HRTEM of a Ti-Au nanoparticle viewed along five-fold axis ([110] direction) in fcc lattice), showing five twins and truncated decahedral shape.



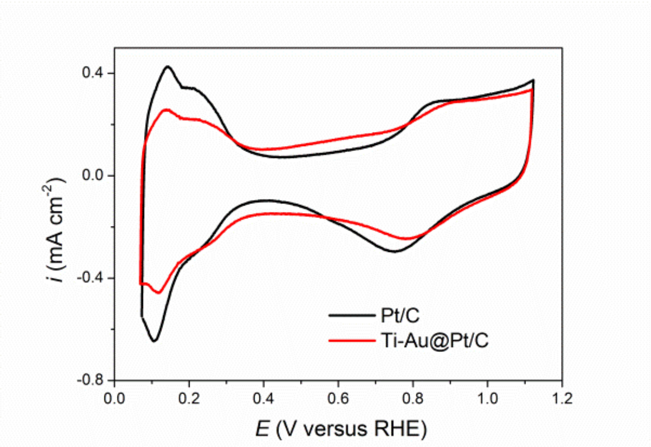
EELS of Ti L_{32} and Au M_{54} edges from area I (red) and area II (blue) in **c**

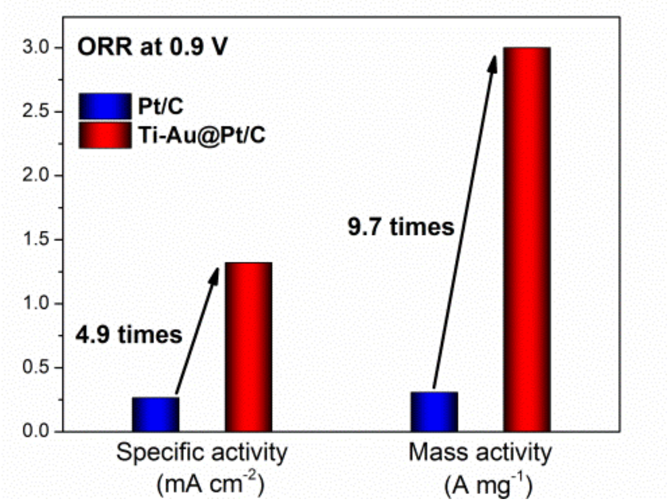
Maps of Ti L_{32} (f) and Au M_{54} (g) edges from the 2D EELS spectrum image, and overlap f and g

Au is at core, **Ti** distributes at the surface of the particles, mainly at the sharp corners

New class of core-shell catalysts

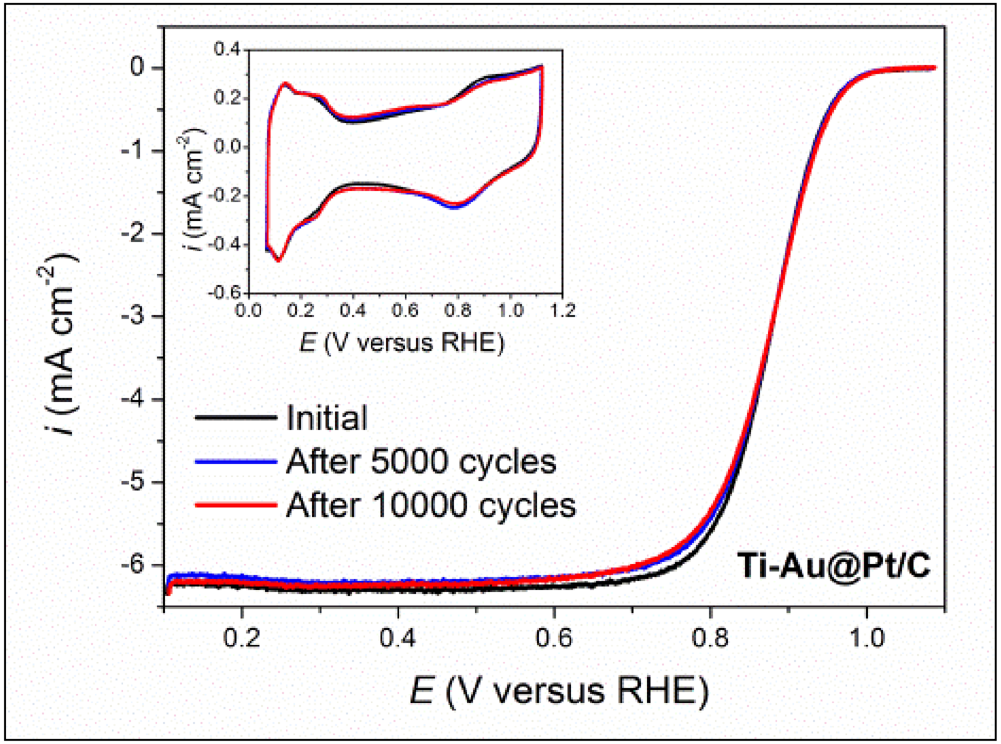
Pt monolayer on TiO_x decorated Au cores





$MA(Pt) = 3A/mg_{Pt}$
$MA(Pt + Au) = 0.34A/mg_{(Pt + Au)}$

ORR activity and durability

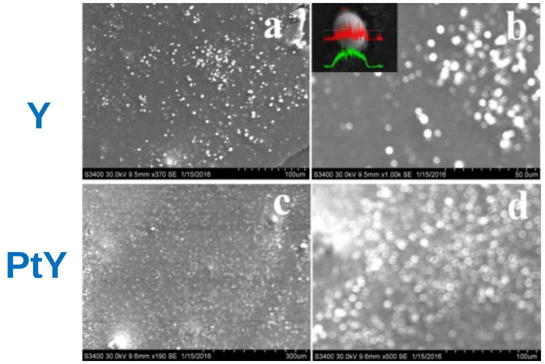


Ti-oxide:
- Controls the amount of Au atoms that segregate on the Pt surface
- destabilizes OH_{ad} on Pt . High durability is expected.

New syntheses from ionic liquids

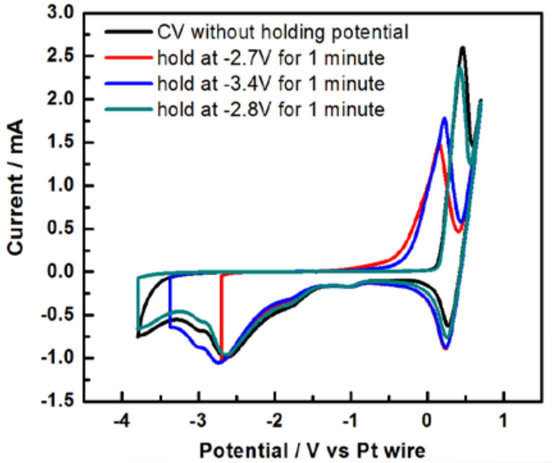
Electrodeposition of Yttrium and Y-Pt alloys from ionic liquids and non-aqueous solvents

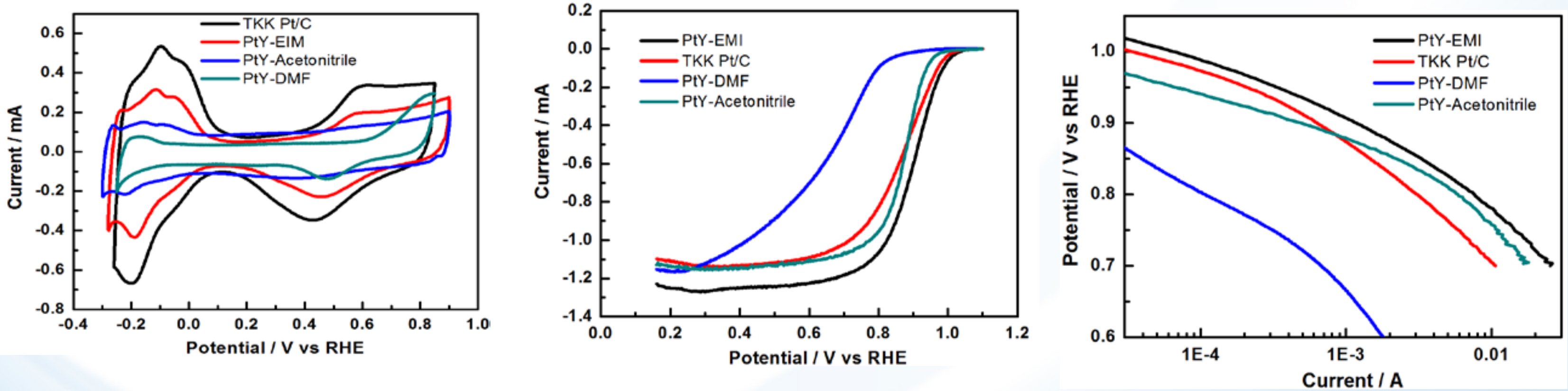
High activity of Pt-Y alloys shown by DFT calculations and sputter deposition catalysts. Norskov et al. Electrodeposition from ionic liquids offers a promising possibility for nanoparticle synthesis.



SEM pictures of electrodeposited Y (a,b) and PtY (c,d). Insert is EDS of an Y particle

The highest activity found for **PtY – EMI** catalyst, larger than for PtY-AN; PtY-DMF or Pt/C TKK.



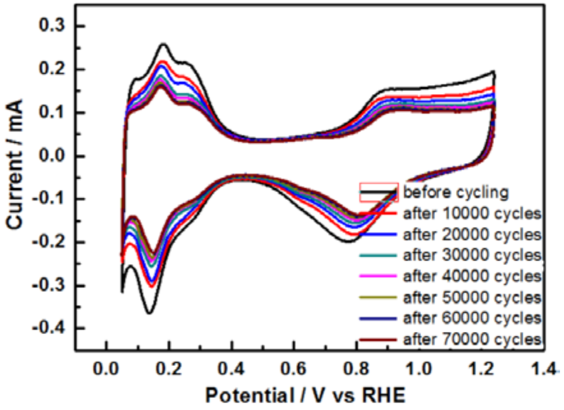


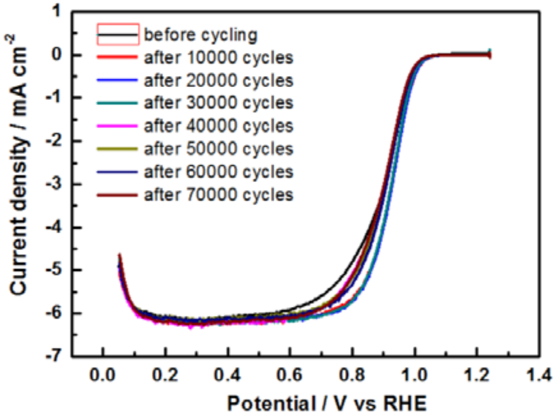
CV in Ar saturated 0.1M $HClO_4$ solution. PtY electrodeposited in 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMI), acetonitrile (AN) and dimethylformamide (DMF).

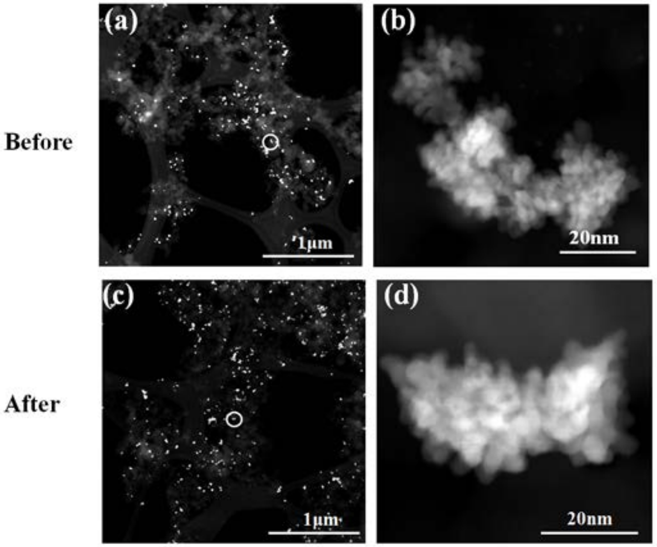
New syntheses from ionic liquids

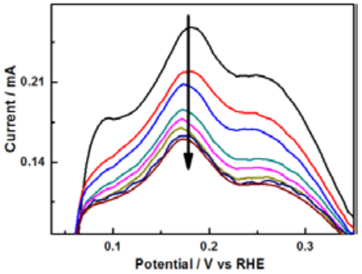
PtY

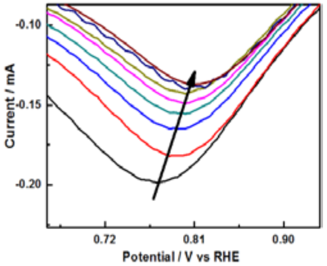
Accelerated test between 0.6-1.1V vs RHE

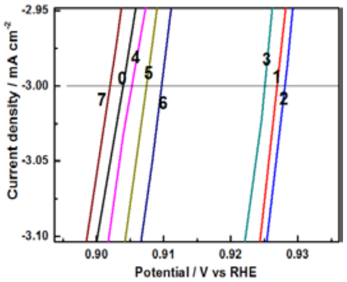




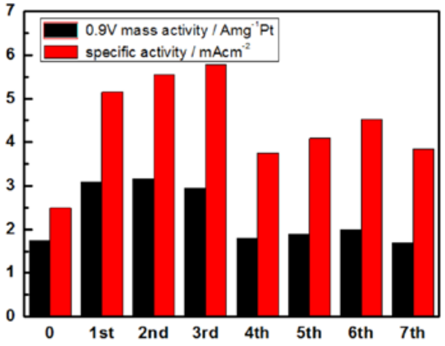








Pomegranate like structure



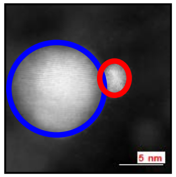
Lattice parameters: Pt:3.917A, PtY:3.865A from EMI-BF4

- Activity: 1.7 A mg_{Pt}^{-1} to 3.0 A mg_{Pt}^{-1}
- Stability: some losses up to 70,000 cycles

TKK Pt/C losses at 10,000 cycles

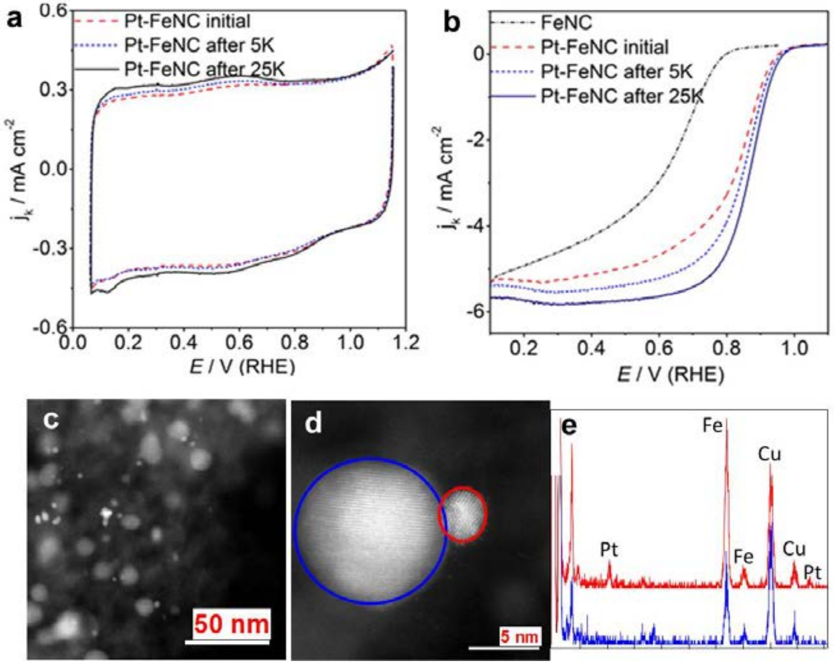
Electrodeposited Janus Nanoparticles for the Oxygen Reduction Reaction

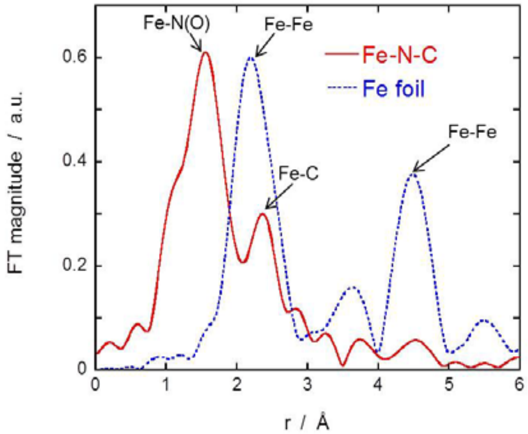
Janus structures - two materials bonded adjacently into a single particle. Synergistic effect increases the durability of the catalyst.



Potential pulse deposition of Pt on 5% Fe-Porphyrin pyrolyzed at 700ºC in NH_3 on graphene. Nucleation of Pt occurs preferentially on Fe.

Pt clusters on Fe-N-C nanoparticles encapsulated in graphene layers make stable catalyst for the ORR. First example in electrocatalysis.





XAS 97% Fe in FeNC

MA=0.69A/mg_{Pt}

STEM-HAADF image and EDS of particles after 25000 cycles show large Fe and small Pt particles.

Janus structures play a bifunctional role of tuning the electronic structure of Pt clusters (synergy of Fe-N-C) increasing durability of the catalyst.

SUMMARY

Optimizing structure and composition of bi-metallic cores can significantly improve Pt ML catalysts.

Refractory metals ca be attractive core components and nitrided can make very stable intermetallic compounds with Pt.

High-performance catalyst Pt –Y alloy can be deposited from ionic liquids

Catalysts with oxidized component preferentially segregated to edges and vertexes, and Janus particle catalysts indicate interesting possibilities for further studies.