ASD2017 - 2nd Area Selective Deposition Workshop

Design and Synthesis of Catalytic Nanoparticles via Area Selective Atomic Layer Deposition

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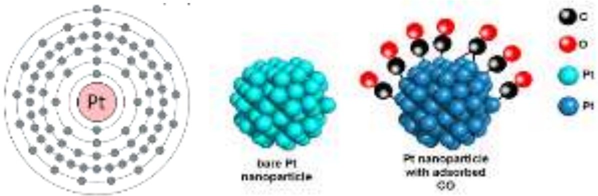
2017-04-21, Eindhoven

Outline

- Catalyst challenges and model catalyst design
- Reactivity, Selectivity, and Stability
  1. Core-shell nanoparticles
  2. Nanotrap Pt/CoO_x structures
  3. Nanofence Pt with active oxides coating structures
- Summary and outlook for selective ALD in catalysis applications

Noble Metal Catalysts

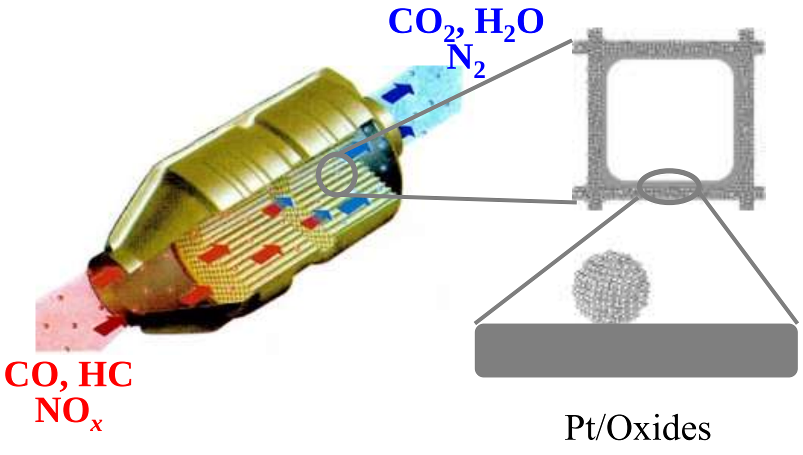


Huge demand for noble metals

-- PGM market report *2016 Nov*

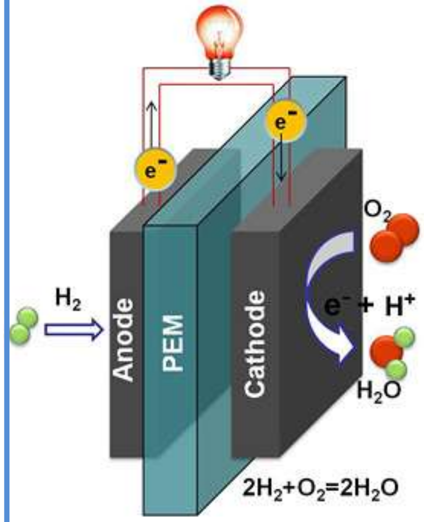
	2014			2015			2016		
	Pt	Pd	Rh	Pt	Pd	Rh	Pt	Pd	Rh
automobile catalyst demand(ton)	97.1	233.2	24.6	101.6	238	23.7	103.3	243.9	24.2
total demand(ton)	186.6	247.9	21.1	204.2	211.6	20.6	199.9	221.9	21
total supply(ton)	160	189.9	19.1	190	200.5	23.5	186.9	201.8	23.1
automobile catalyst percentange(%)	38.7	70	80.4	39.4	82.6	81.4	40	80.9	81.2

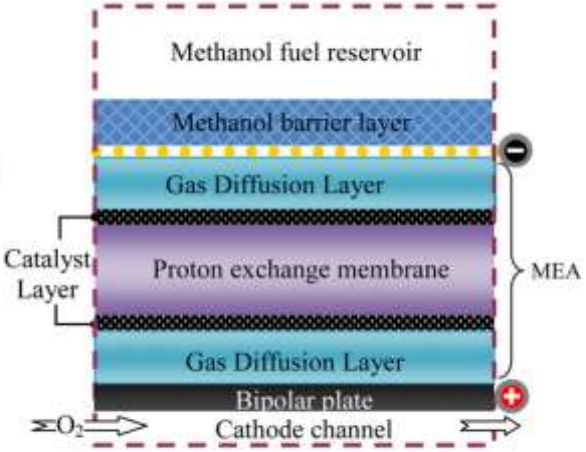
Catalysis for environment



CO, HC and NO oxidation

Catalysis for energy



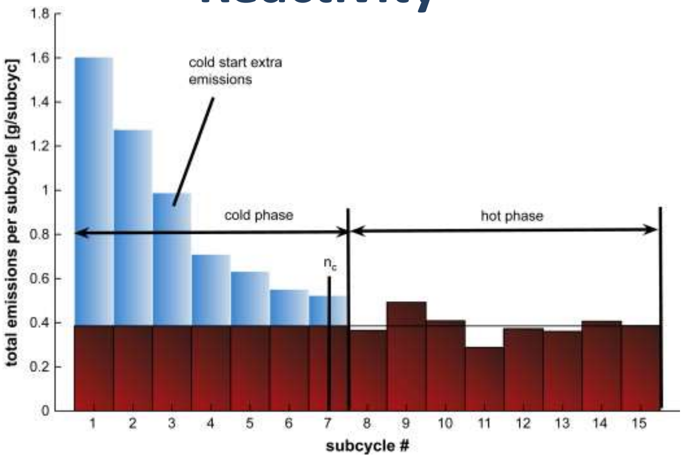


ORR, MOR, OER, HER

Chem. Rev., 2016, 116, 3594; Chem. Soc. Rev., 2015, 44, 2168; Chem. Soc. Rev., 2008, 37, 2204

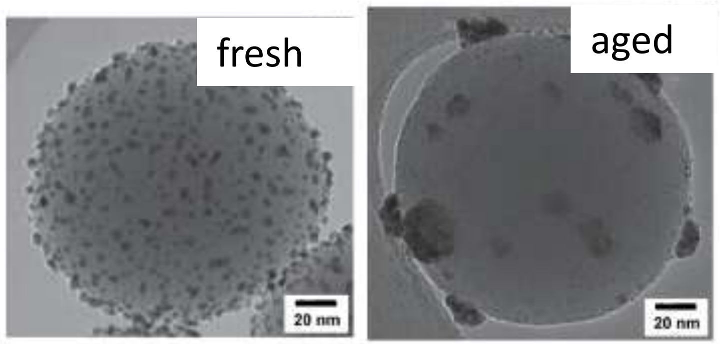
Challenges in catalysis

Reactivity



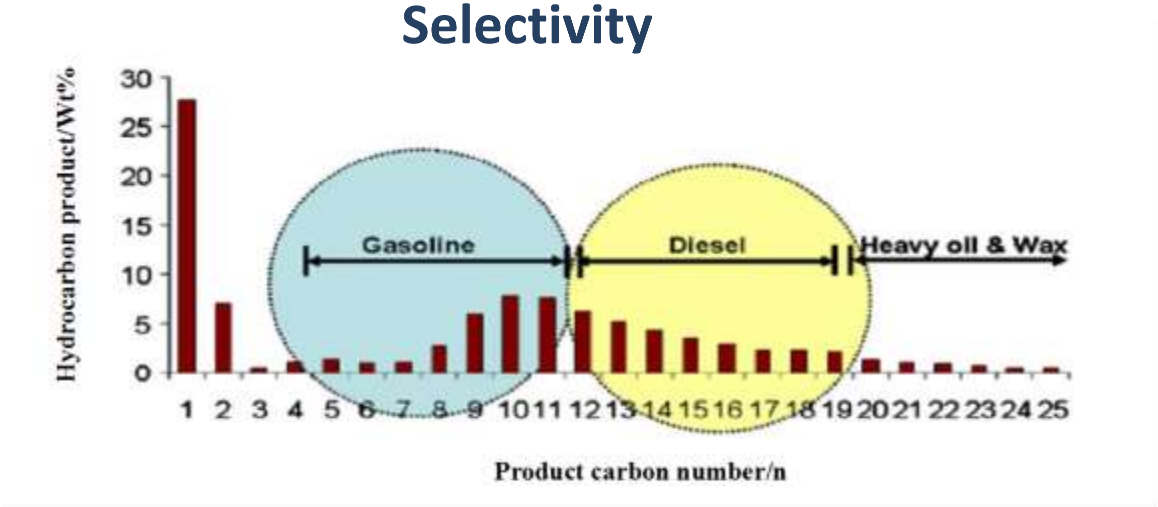
Cold start

Stability



Sintering and coking

Selectivity

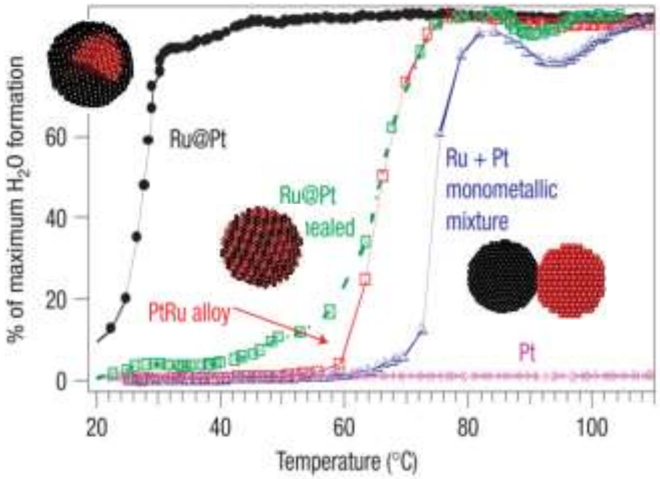


carbon cycling reactions

Atmospheric Environment, 2009, 43, 996

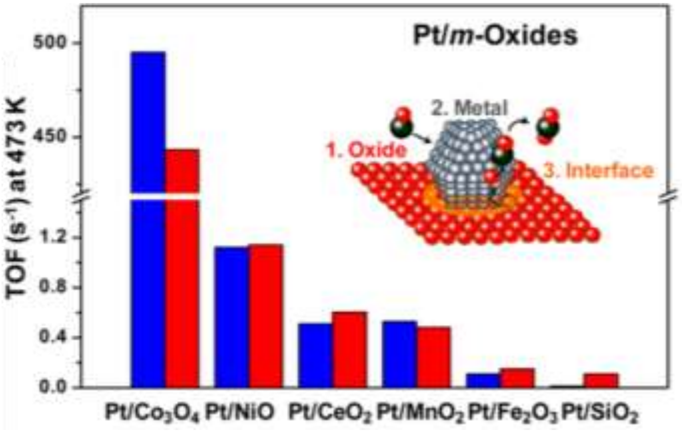
Design for Activity

nanostructures



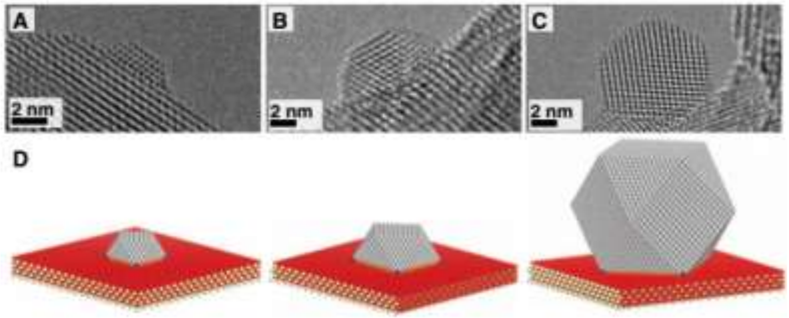
Nat. Mater., 2008, 7, 333

strong metal-oxide interactions

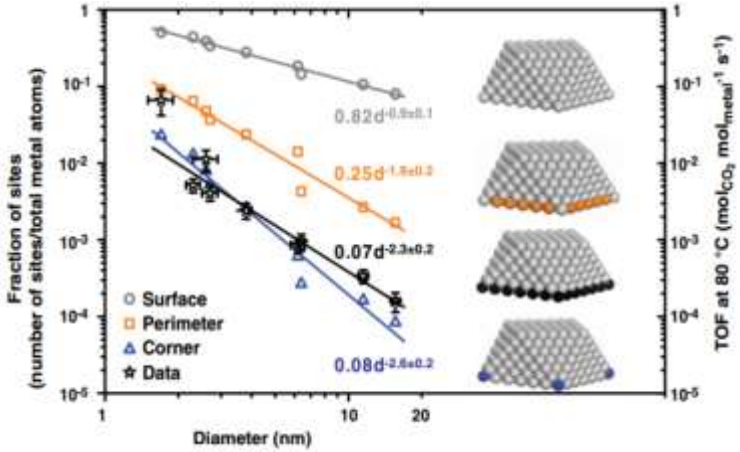


J. Am. Chem. Soc, 2013,135,16689

selective decoration

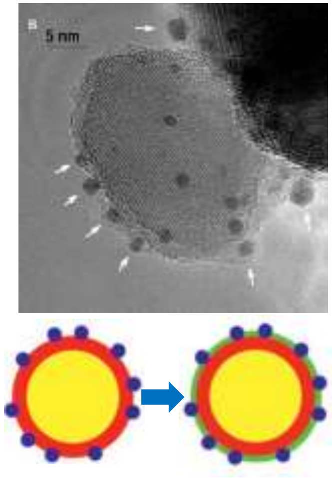


Science, 2013,341,771

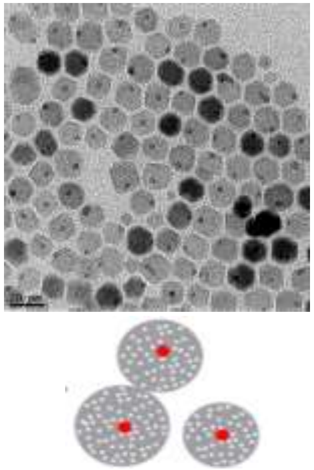


Design for Stability

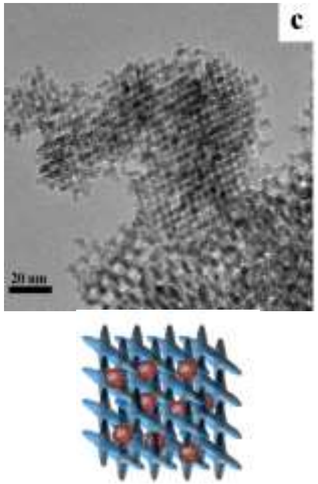
physical separation to eliminate migration



Catal. Lett. 2011

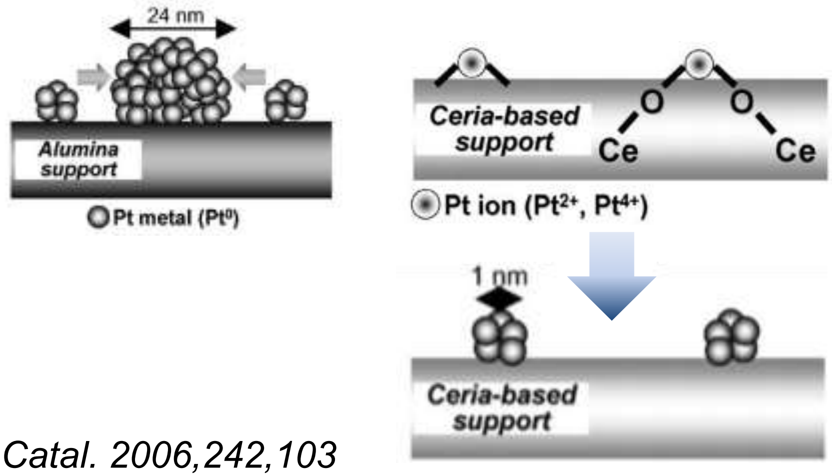


J. Phys. Chem. C, 2008



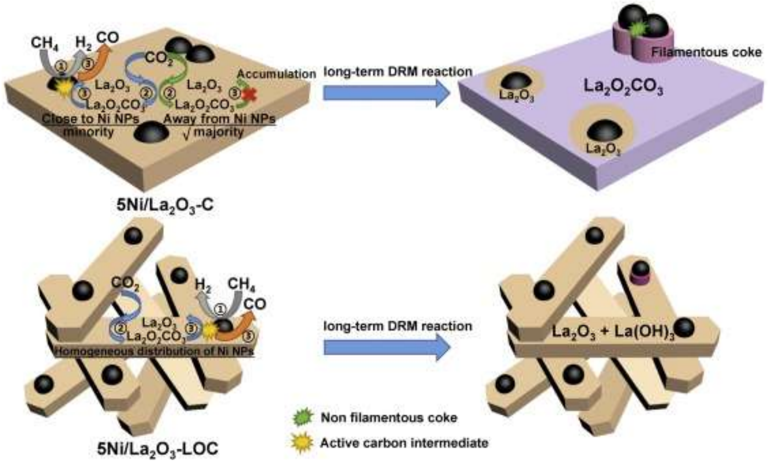
J. Phys. Chem. C 2013

metal oxide anchoring



J. Catal. 2006,242,103

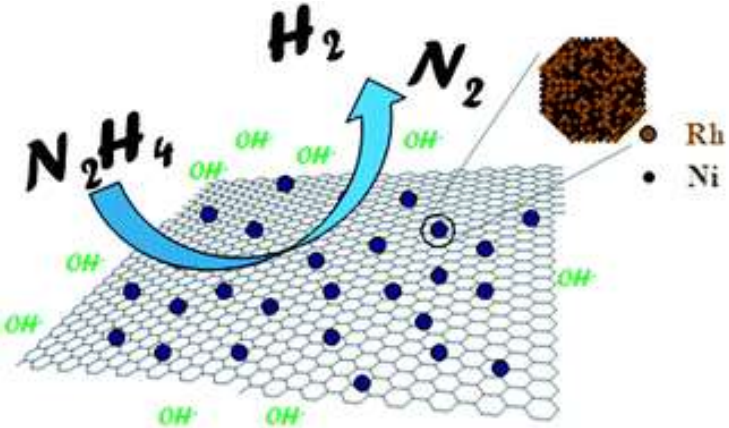
coking inhibition



Applied Catalysis B, 2017, 202, 683

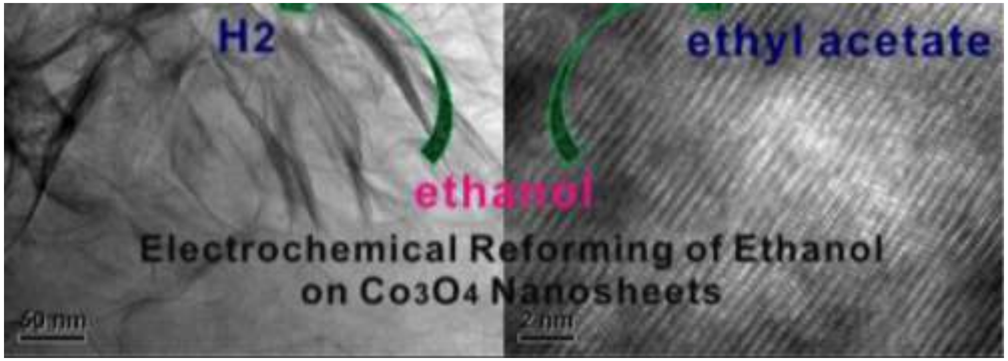
Design for Selectivity

alloys



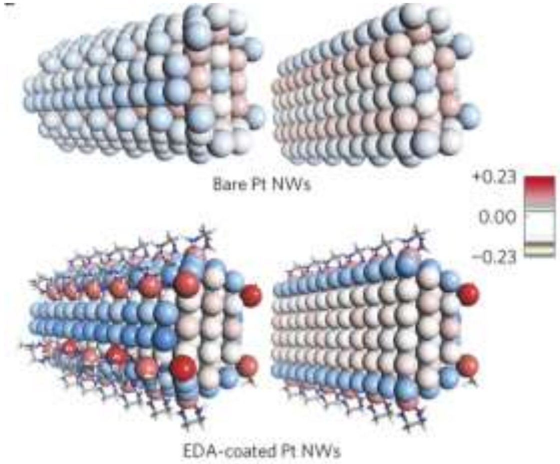
Energy Environ. Sci., 2012, 5, 6885

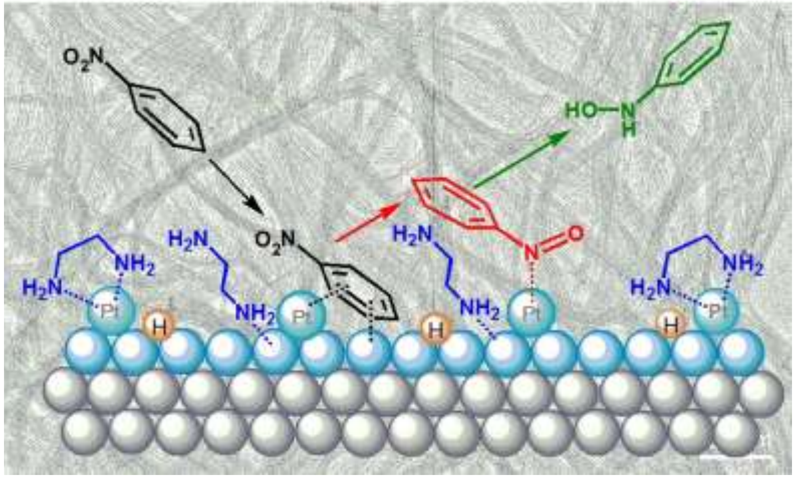
Facets preference



ACS Cent. Sci., 2016, 2 (8), pp 538–544

Interfacial electronic transfers

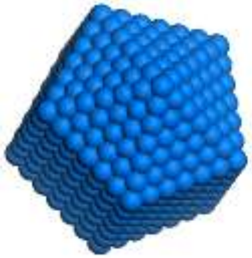




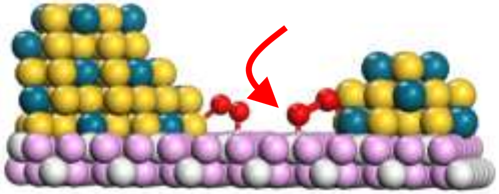
Nature Materials, 2016, 15, 564

Precise control of catalyst structures

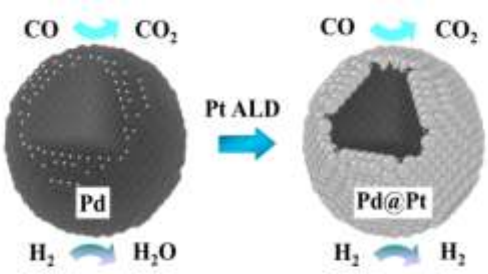
Noble metals



Nanoparticle

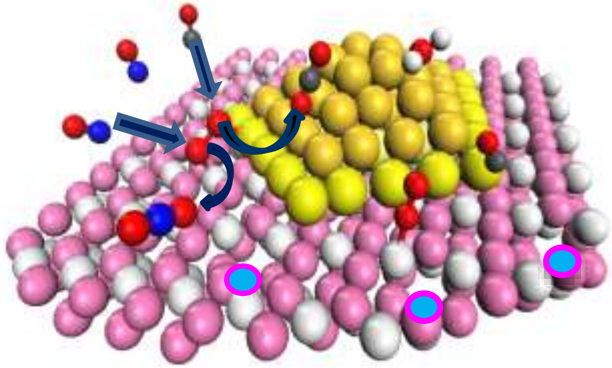


Size and composition

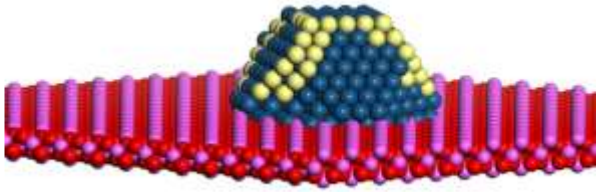


Core shell structure

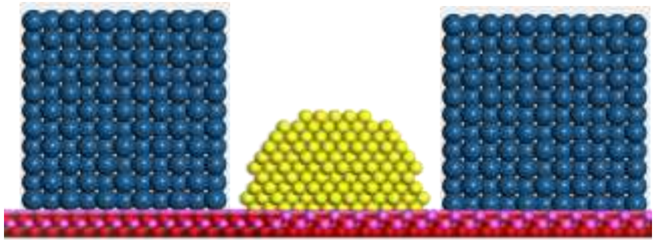
Metal oxides



Active oxide support



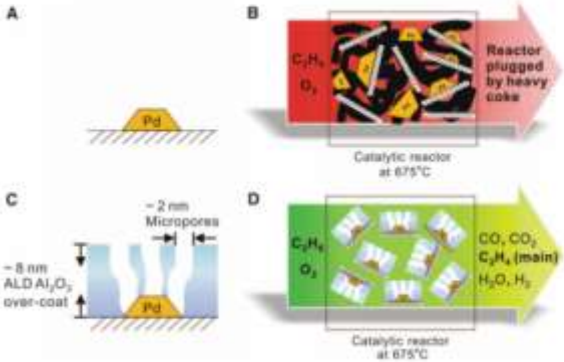
Oxide coating



Interface

Catalysts Design via ALD

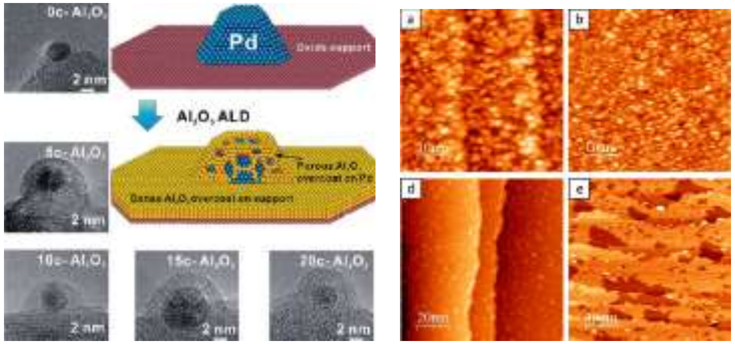
Post thermal treatment



Coking and sintering-resistant enhanced in oxidative dehydrogenation of ethane

Science, 2012,335,1205

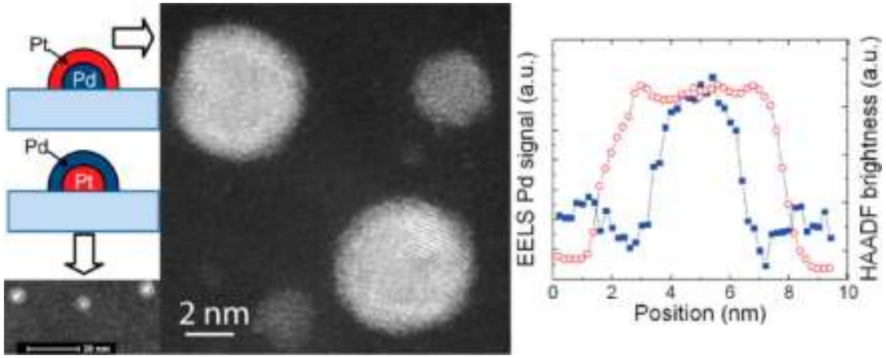
Porous coating



Stabilize the catalysts in methanol decomposition et al.

Chem. Mater. 2012,24,2047 Chem. Mater. 2014,26,6752

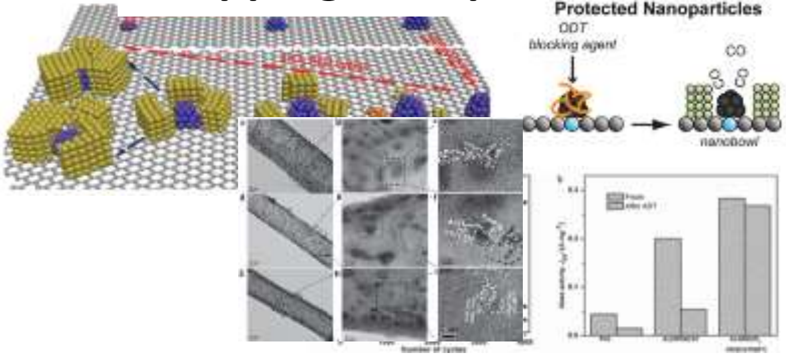
Selective ALD of core-shell structures



Temperature & partial pressure adjustment

Chem. Mater., 2012, 24, 2973

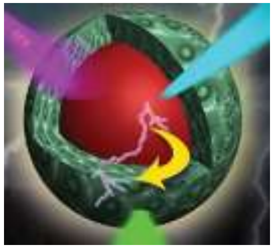
Selective ALD of trapping nanoparticles



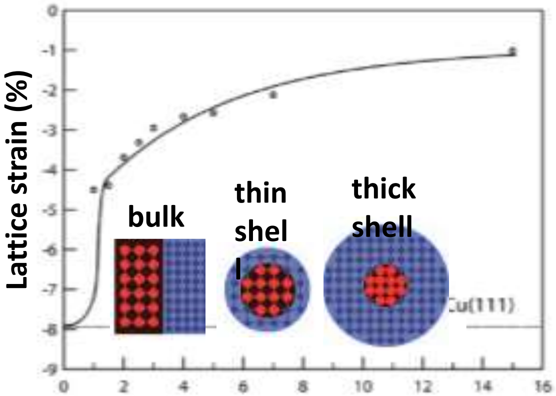
Stabilize Pt catalyst with nanotraps in ORR

J. Phys. Chem. C, 2012,116,7748, Adv. Mater. 2015,27,277

Core-shell Bimetallic Catalysts

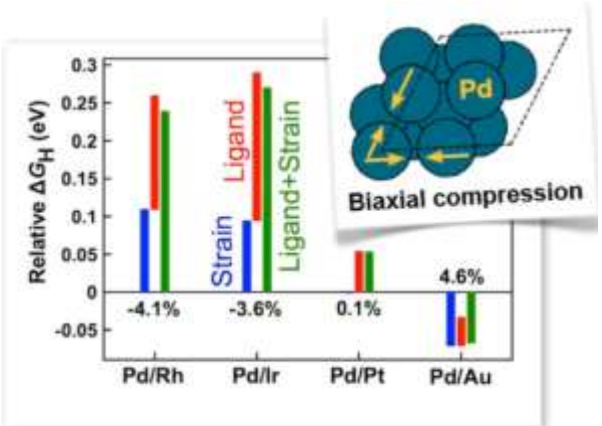


Lattice strains

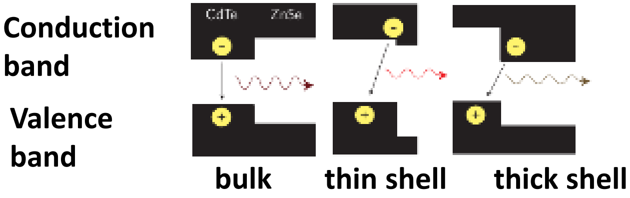


Alayoglu et al. Nat Mater. 2008

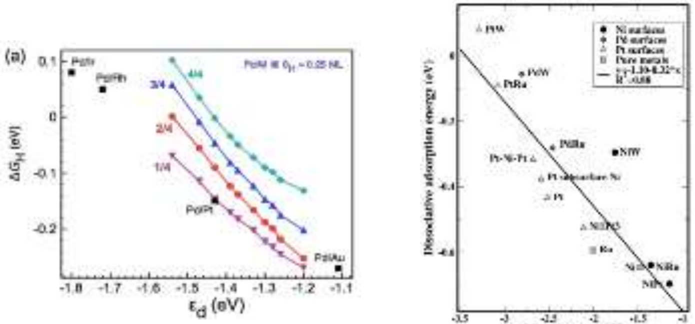
Ligand (Electronic) effect



Maark et al. J. Phys. Chem.C. 2014



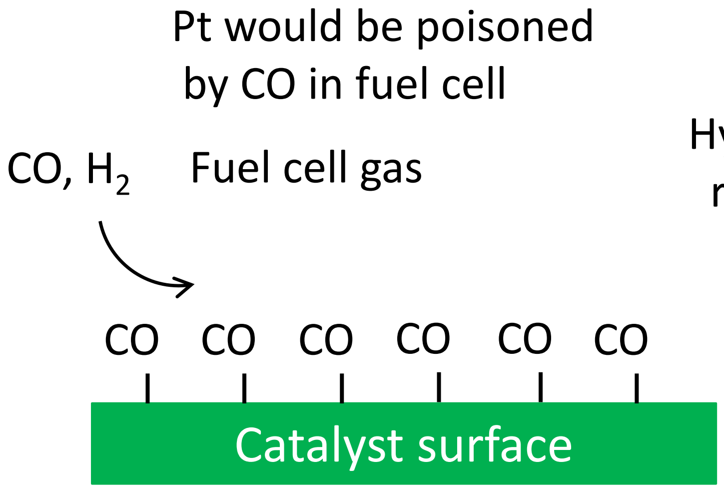
Kar et al. Nanoscale. 2012



Norskov et al. Phys. Rev. Lett. 2004

Modification of electronic & chemical properties

Preferential Oxidation of CO (PROX)

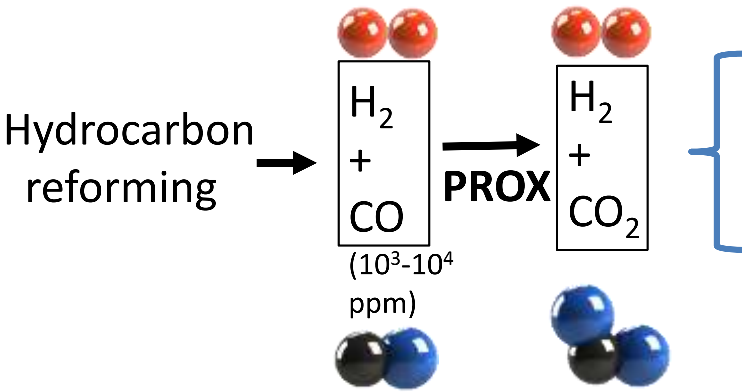


Pt would be poisoned by CO in fuel cell

CO, H_2 Fuel cell gas

CO CO CO CO CO CO

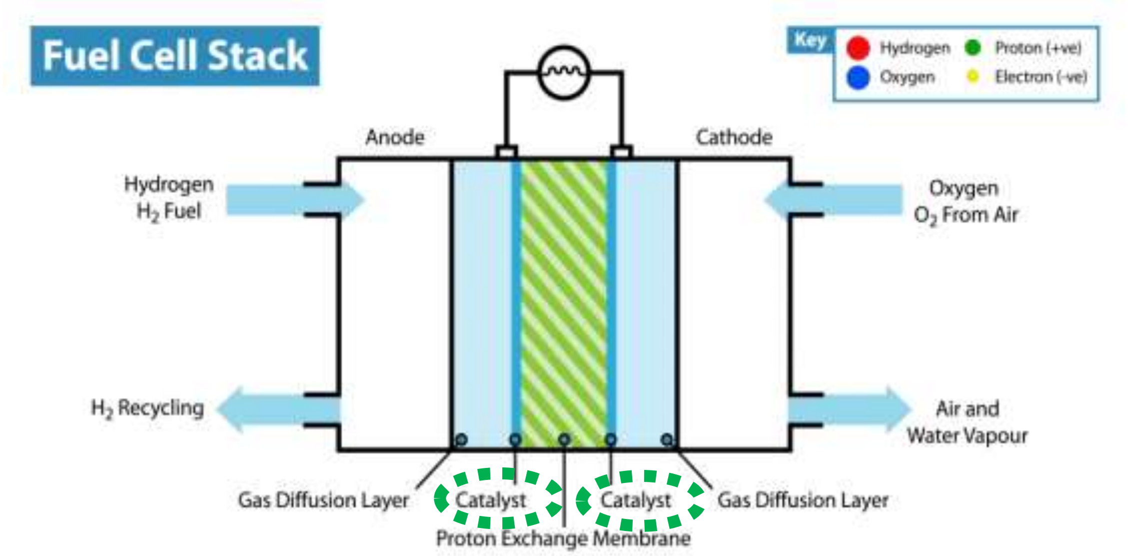
Catalyst surface

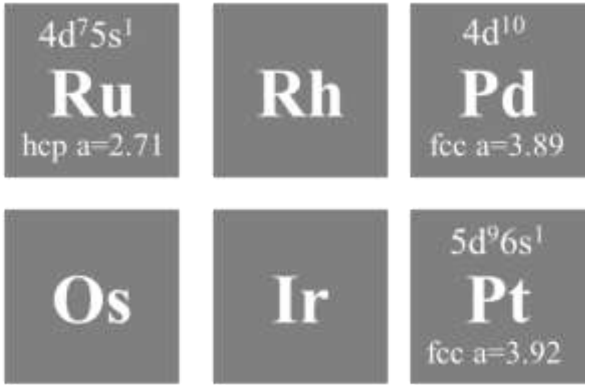


Hydrocarbon reforming → H_2 + CO (10^3-10^4 ppm) $\xrightarrow{\text{PROX}}$ H_2 + CO_2

High reactivity
CO: <100ppm

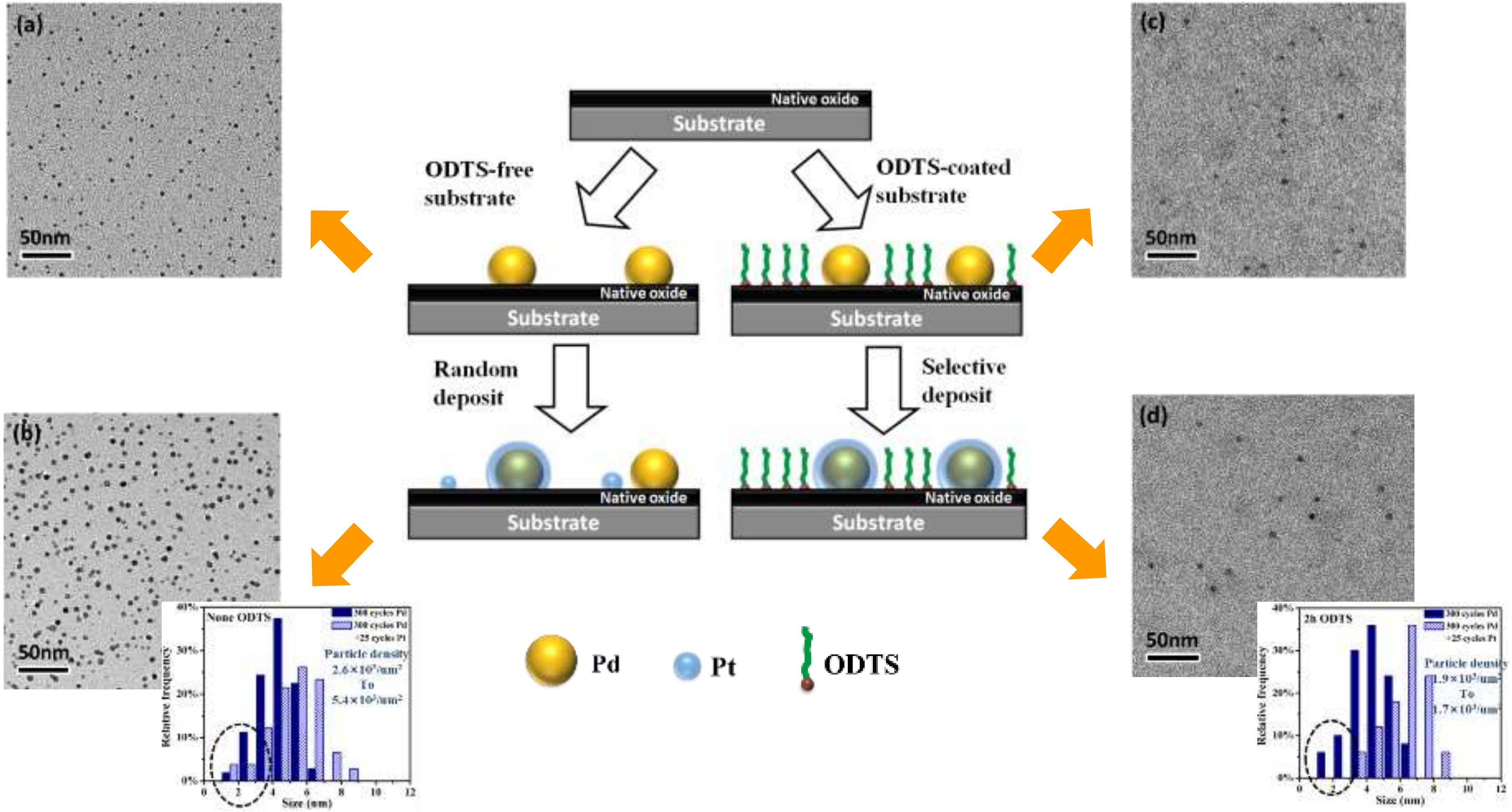
High selectivity
no H_2 consumption





Strategy for fabricating core shell NPs

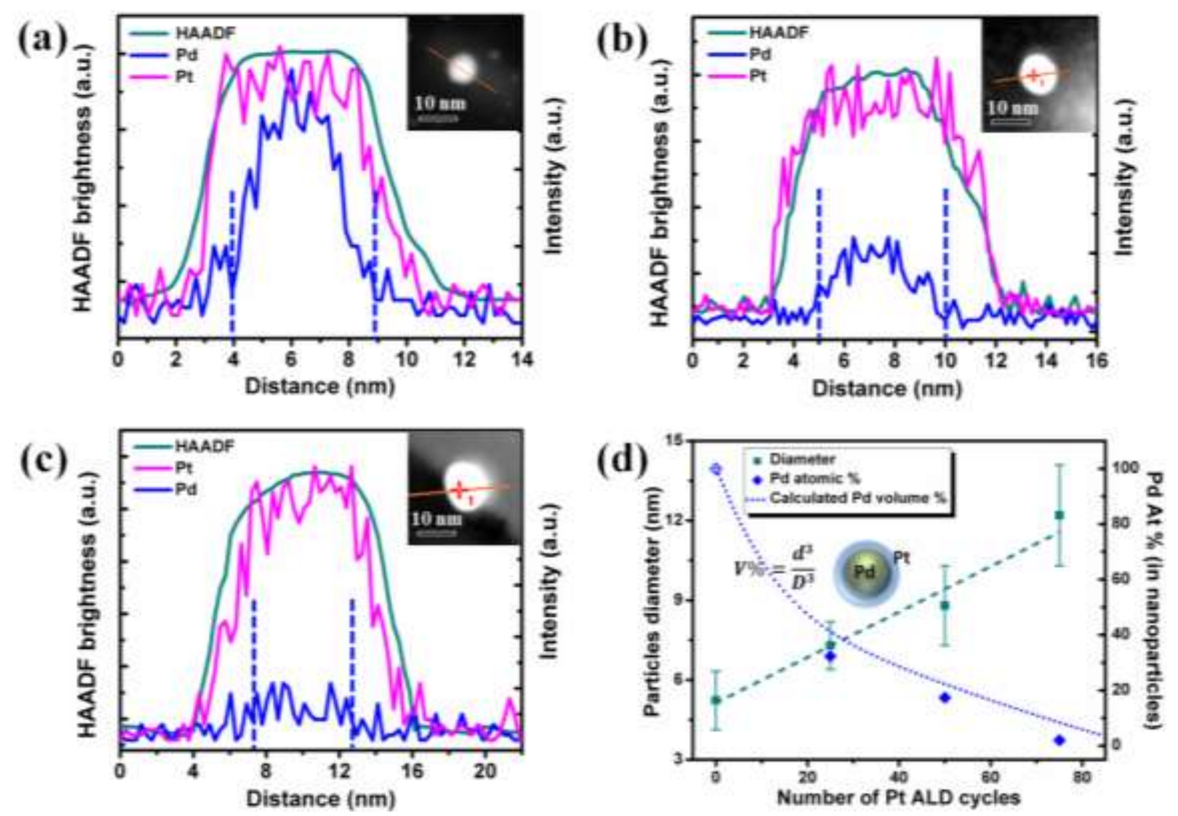
utilizing area selective ALD to fabricate core shell NPs with regular ALD recipes

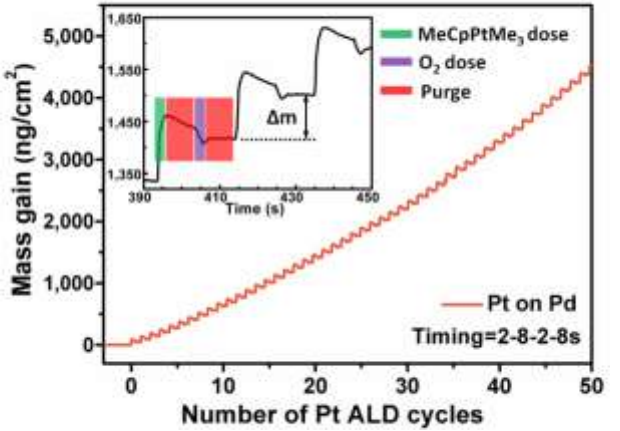


Sci. Rep. 5, 8470, 2015

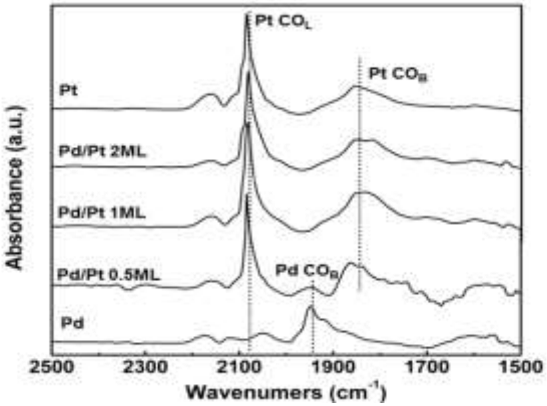
Size and composition control

The size and composition of the core shell NPs can be controlled precisely by varying the ALD cycles





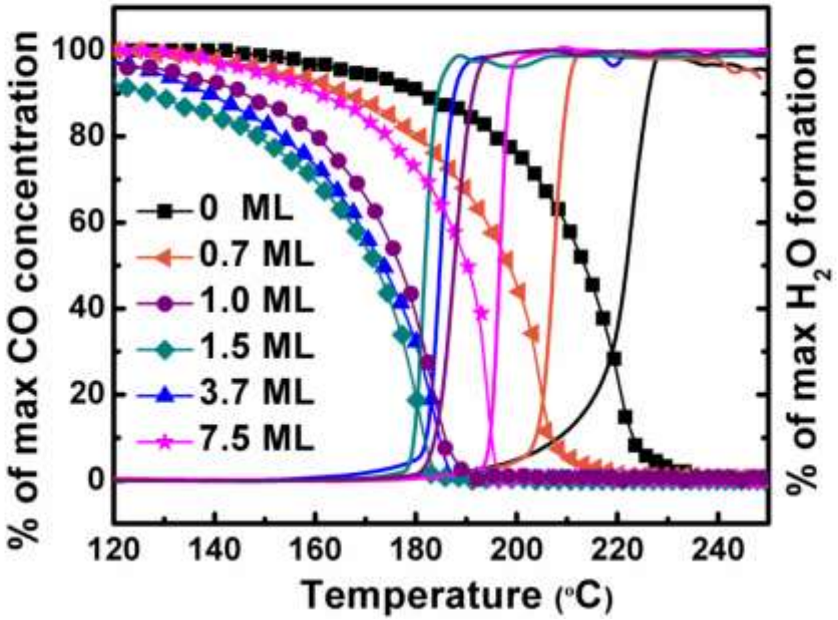
In-situ QCM

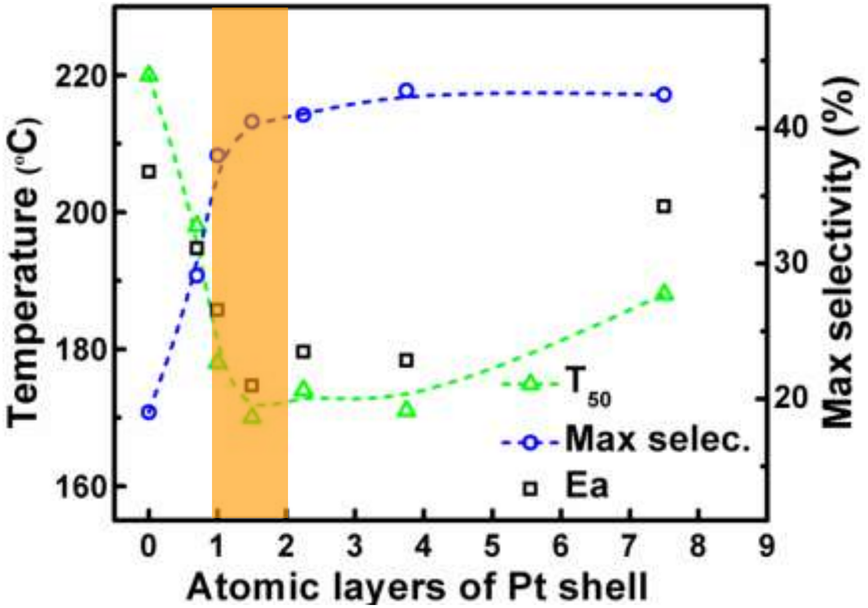


CO FTIR

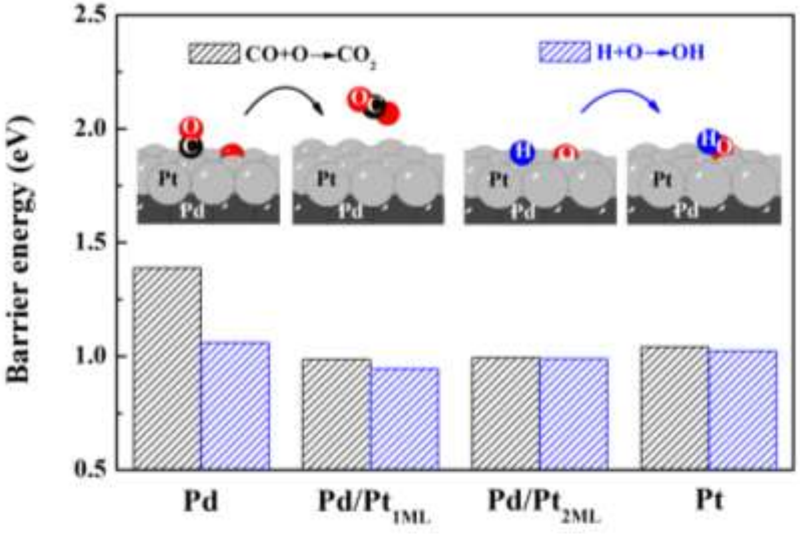
Performance towards PROX reaction

CO-tolerant: $CO+H_2+1/2\ O_2 \rightarrow \boxed{CO+H_2O}$ **PROX**: $CO+H_2+1/2\ O_2 \rightarrow \boxed{CO_2+H_2}$



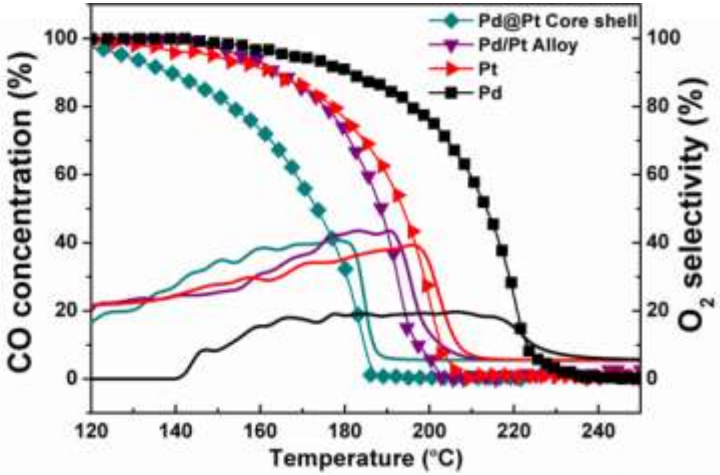


- A monolayer of Pt shell shows significant improved catalytic performance
- Activation energy for CO oxidation of ~ 1 Pt ML NPs has lowest value, suggesting lower CO oxidation barrier



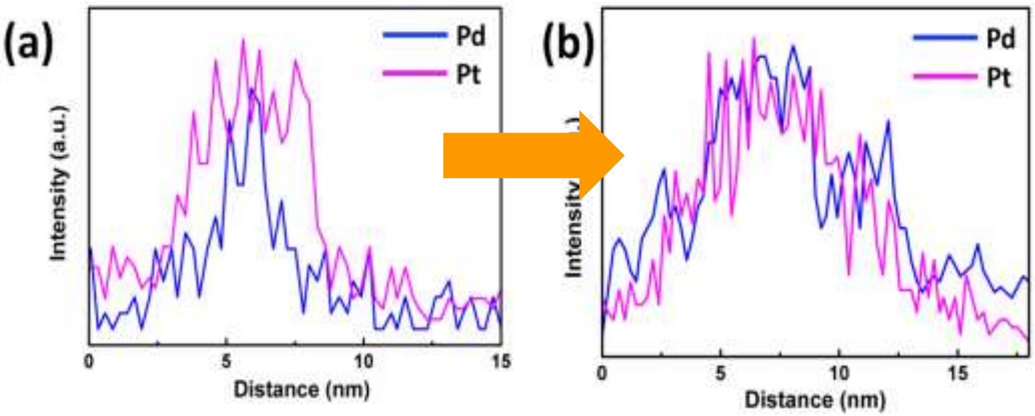
ChemCatChem. 2016, 8, 326

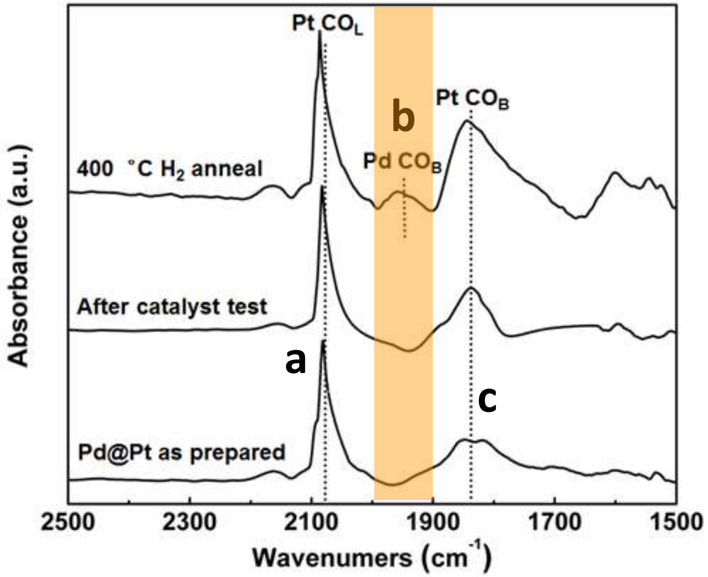
Structure Stability in Redox Environment



As prepared

400°C treatment in H_2 environment

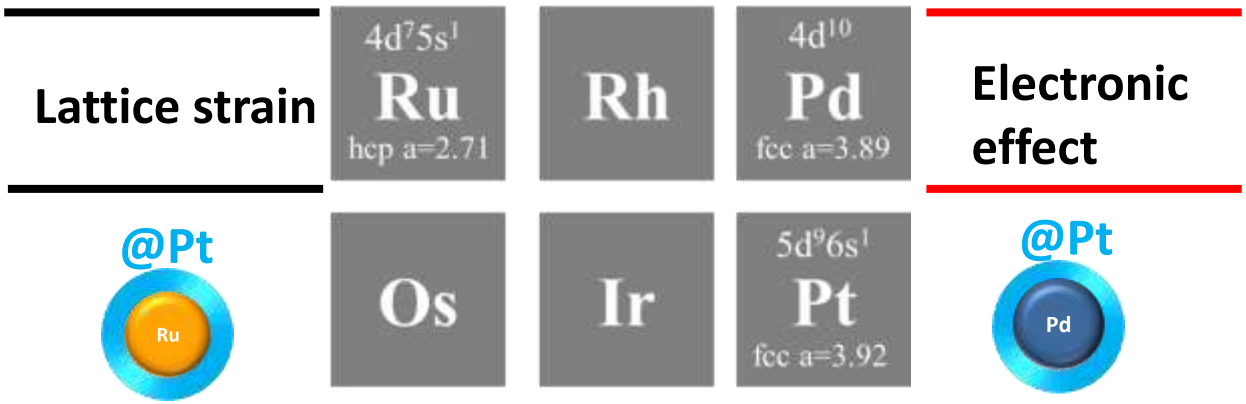




- Desired nanostructure of bimetallic Pd@Pt NPs could promote the performances of PROX reaction
- Pd@Pt structure remains intact after PROX catalytic process

Ru/Pt bimetallic catalysts for PROX

Noble bimetallic core shell nanoparticles

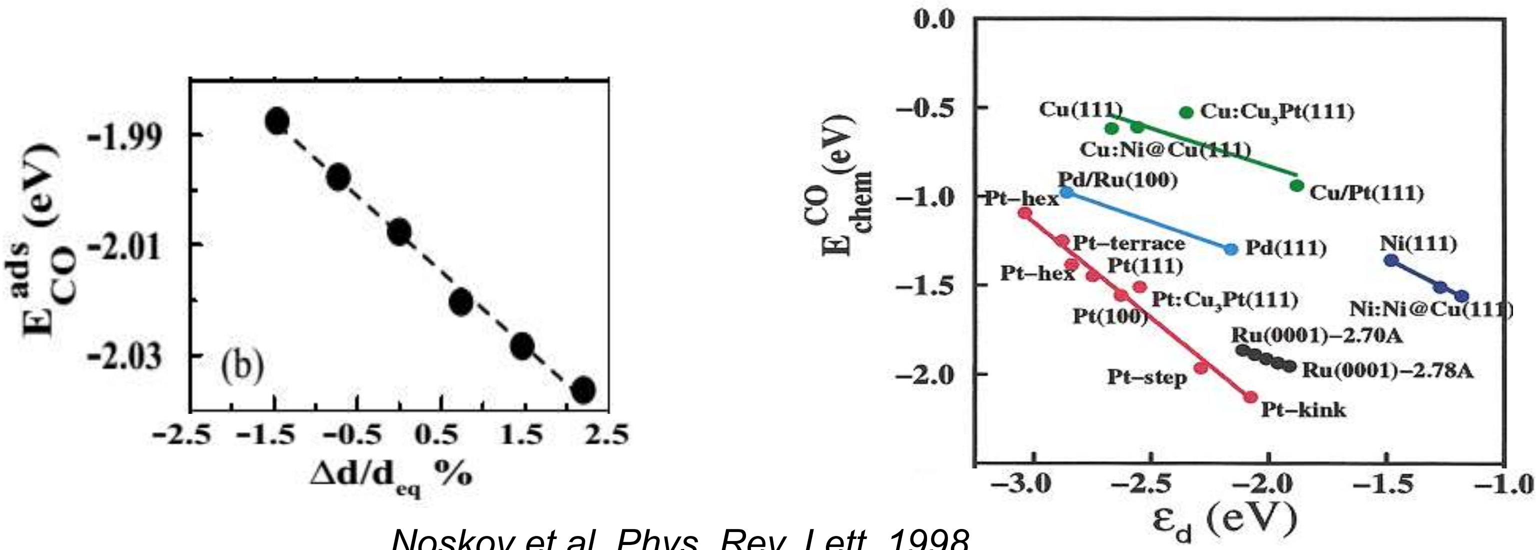


Lattice strain

Electronic effect

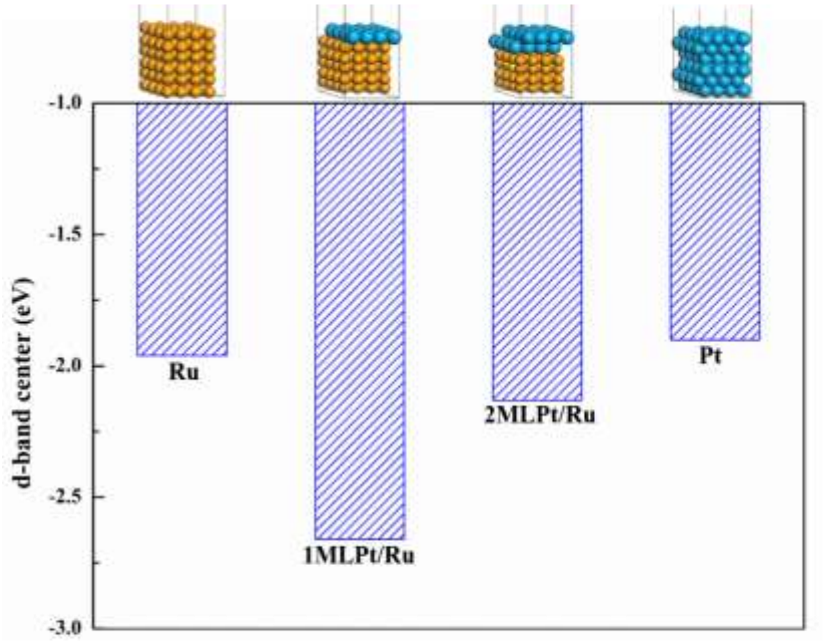
Pd@Pt : lattice matched, core shell interaction

Ru@Pt : mismatched crystal constant, lattice strain factor

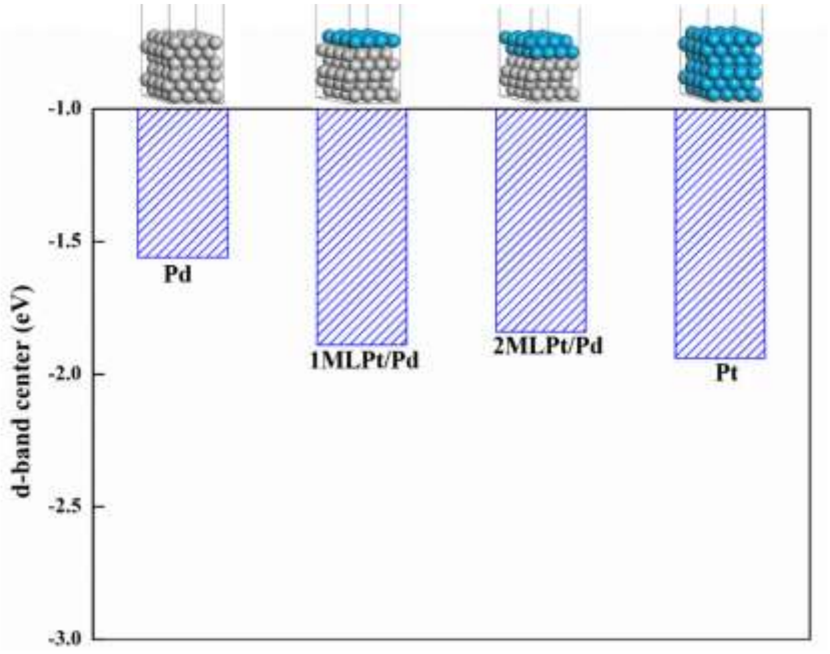


Noskov et al. Phys. Rev. Lett, 1998

d-band Center Comparison

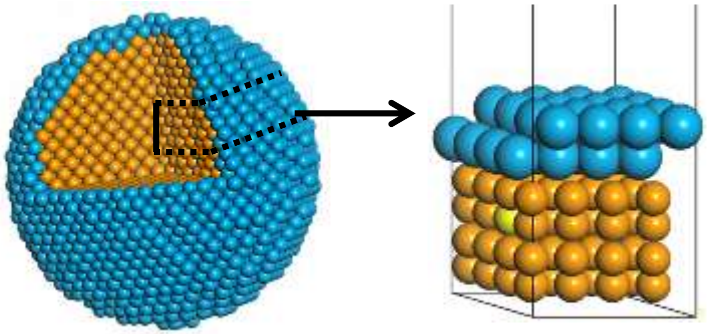


Pt (111) on Ru (001)

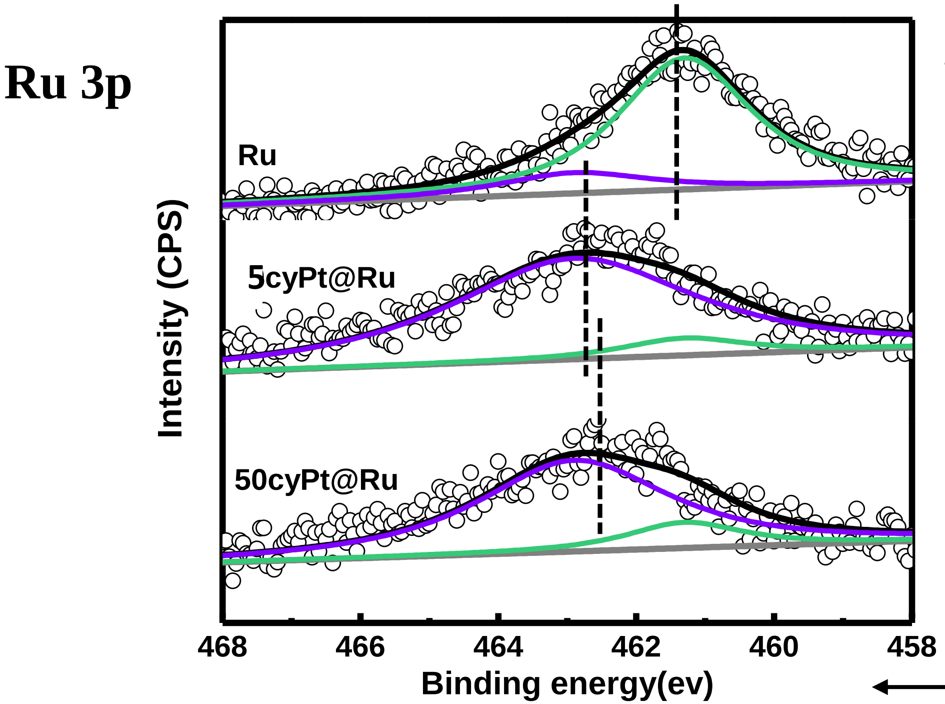


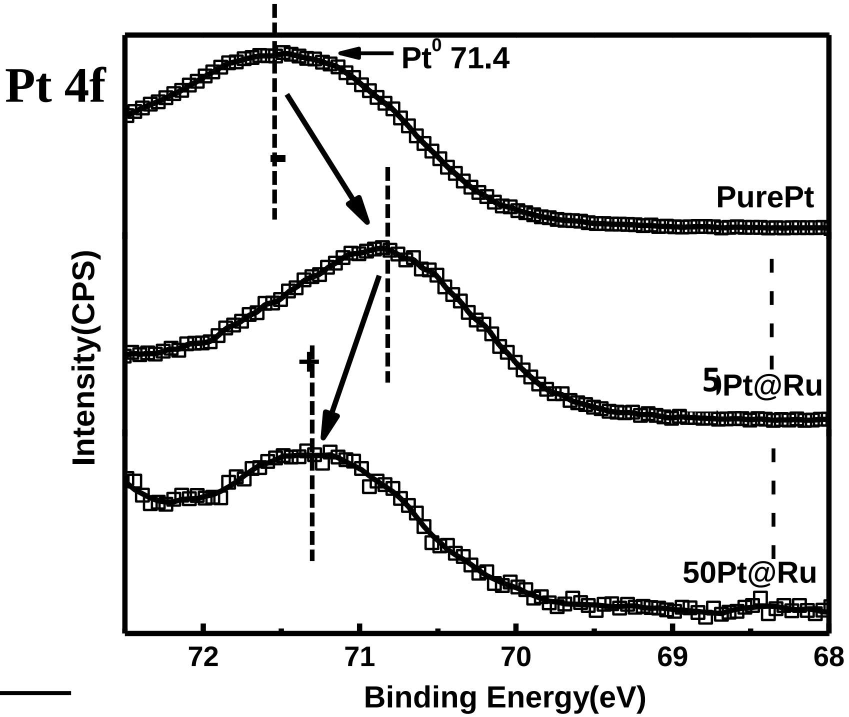
Pt (111) on Pd (111)

- Interaction strength of the catalytic surface with the adsorbates (CO in this reaction) is relevant to the d-band center, negative shift of the d-band center means CO adsorption weakens
- Compared to Pd@Pt, d band center change is significant on Ru with 1 ML of Pt



Electron modification





Electron loss of Ru

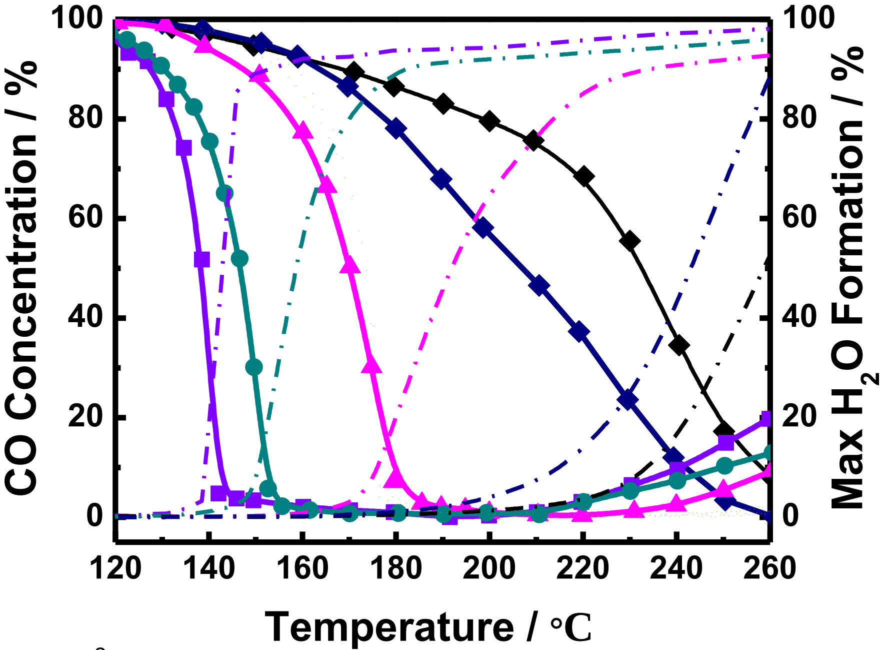
+ positive shift

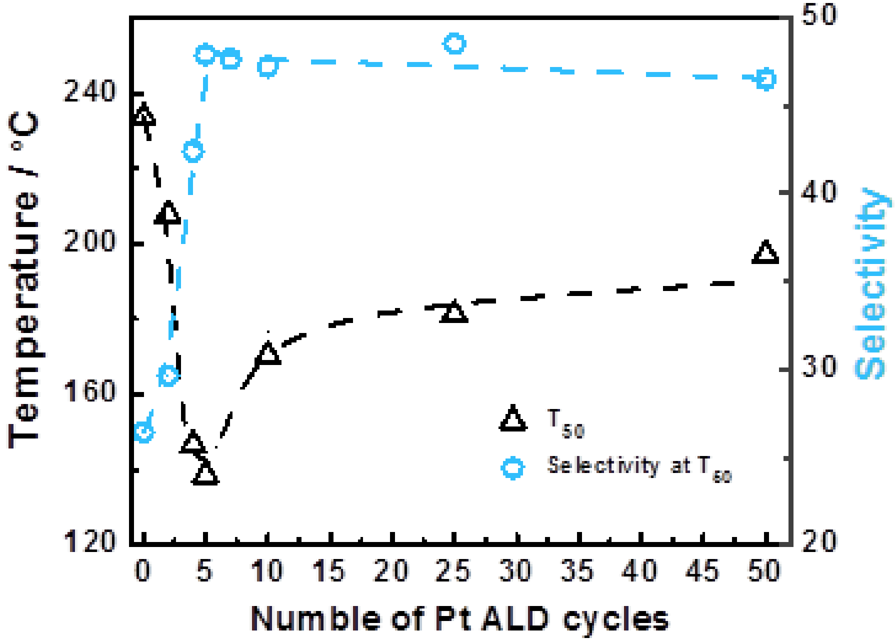
- Down shift

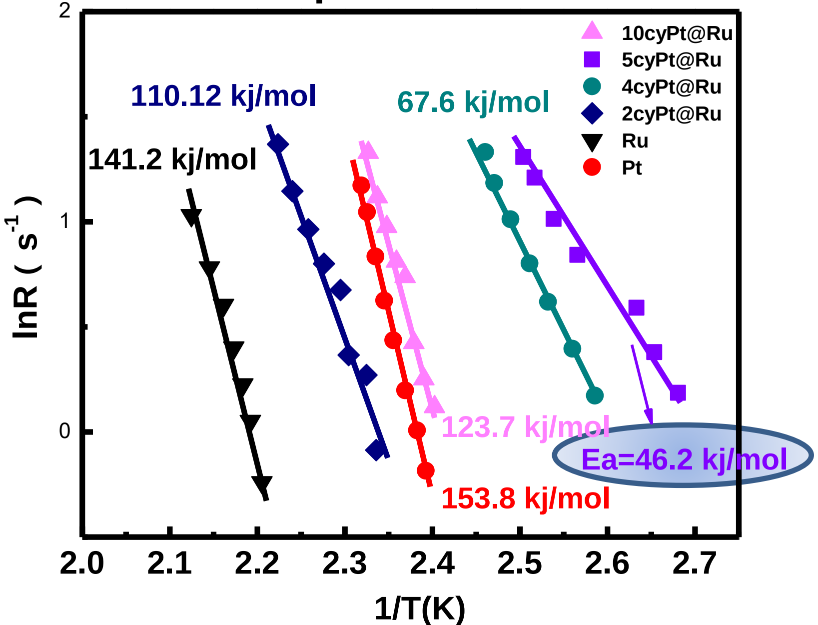
Surface modification of Pt

- Electron transform occurs at the interface of Ru/Pt, from Ru to Pt.

Catalytic activity measurement







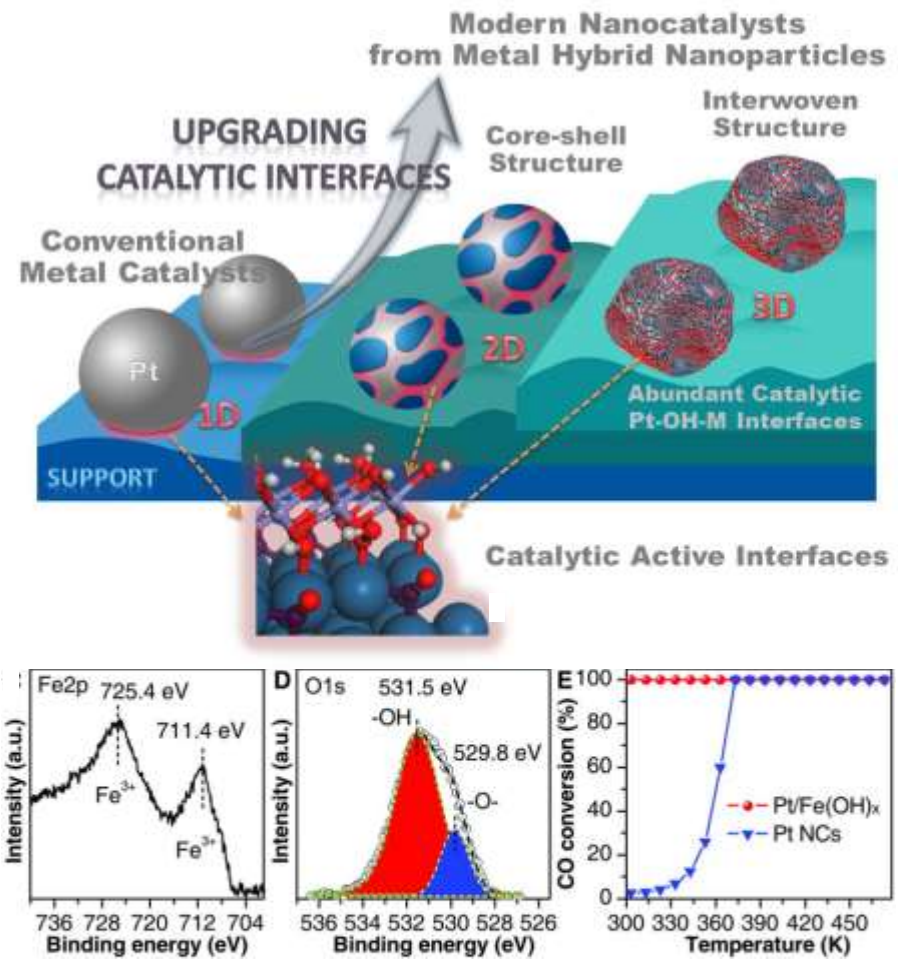
Activation energy calculation

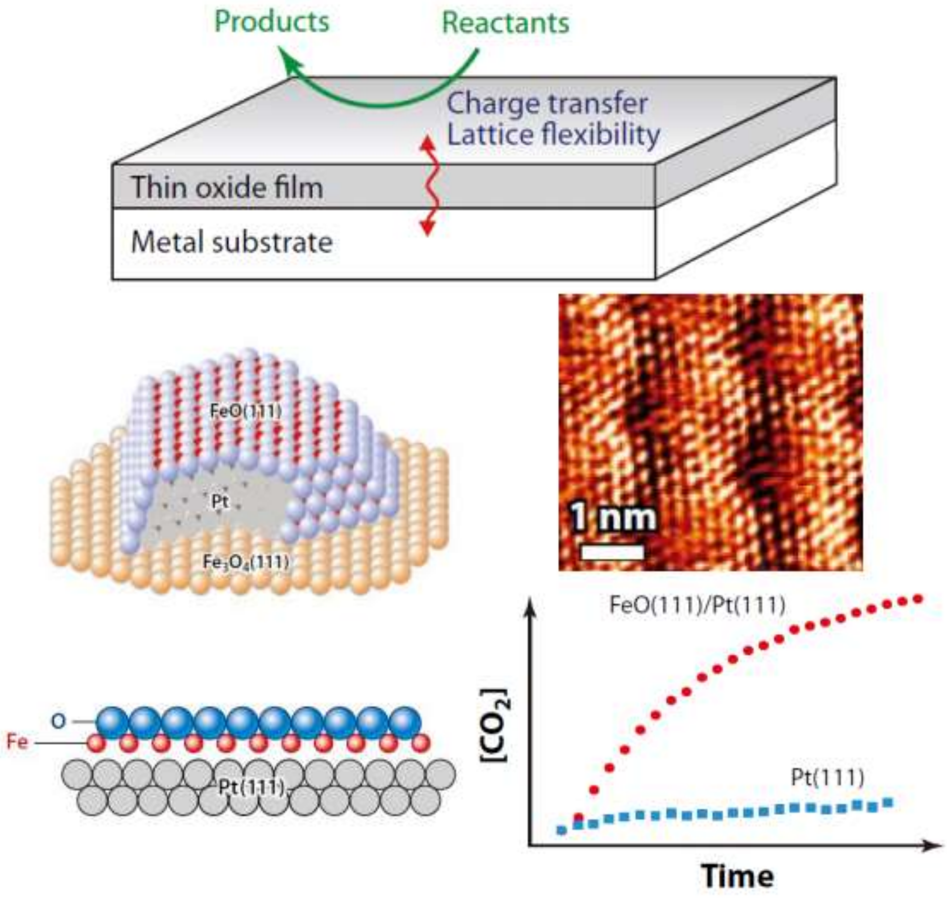
Ref: Nat. Mater., 2008, 7, 333,
Ru@Pt, 1~2 layers Ea=129.4kj/mol

~5 cycle of Pt (less than a monolayer) shows significant improvement of catalytic activity

Metal-oxide interaction

- **metal-oxide interface**



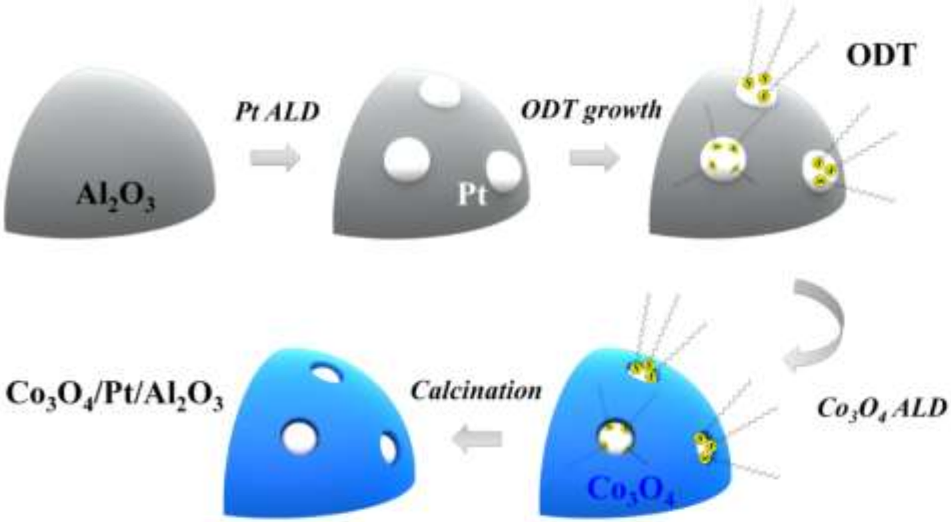


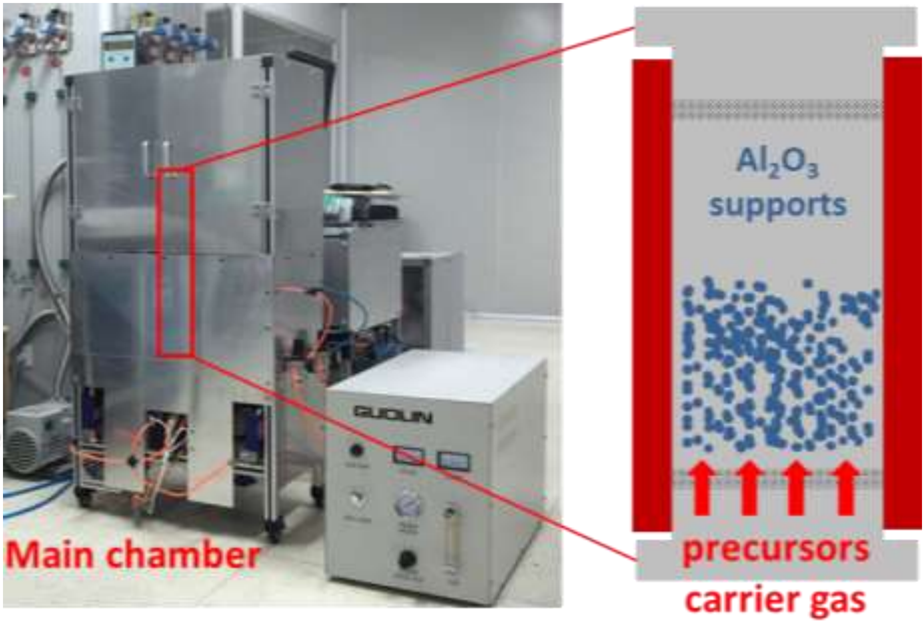
Science, 2014, 344, 495

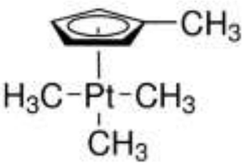
Angew. Chem. Int. Ed., 2010, 49, 4418

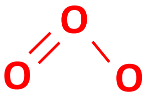
Pt and Co_3O_4 ALD Processes

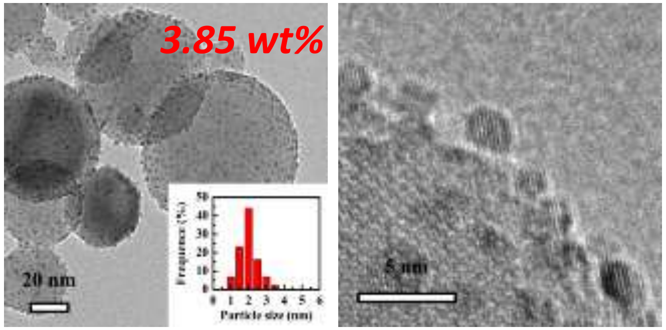
Home made fluidized ALD reactor for powder ALD



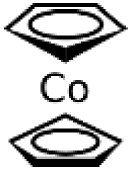


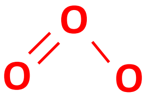


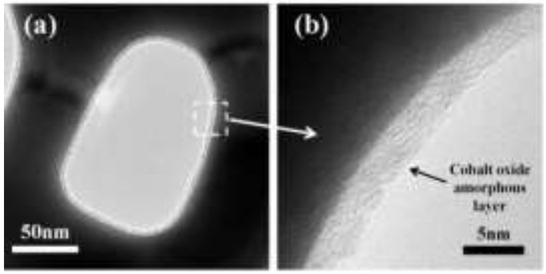




Pt ALD (300 ºC)







Co_3O_4 ALD (150 ºC)

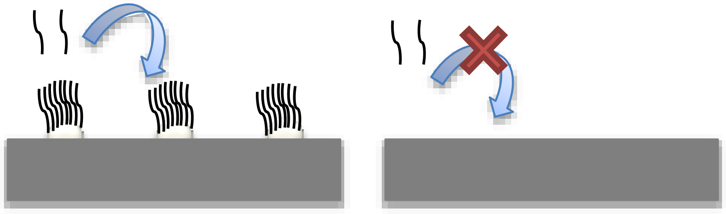
Sci Rep,2015,5,8470

ACS AMI Adv., 2015, 7, 422

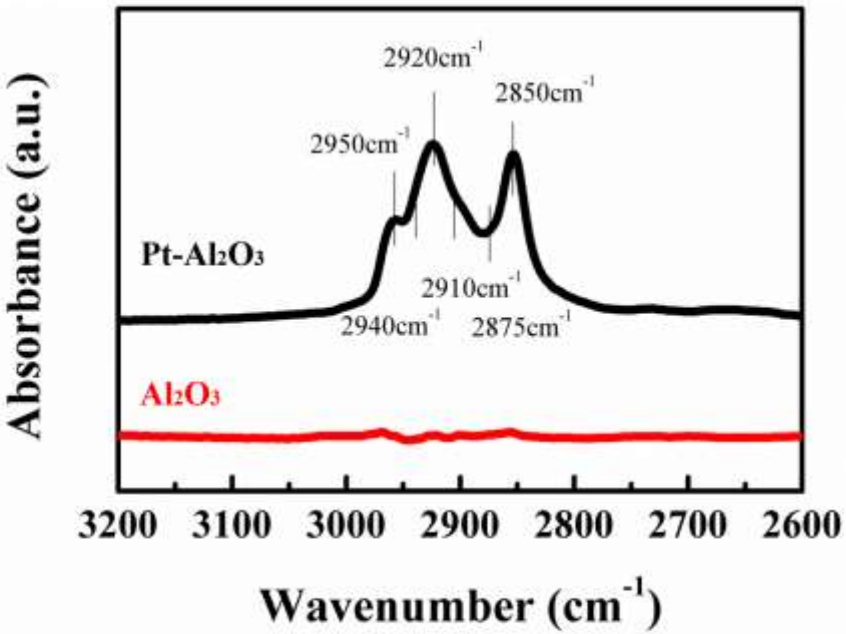
Selective Growth of ODT and Co_3O_4

ODT selective growth

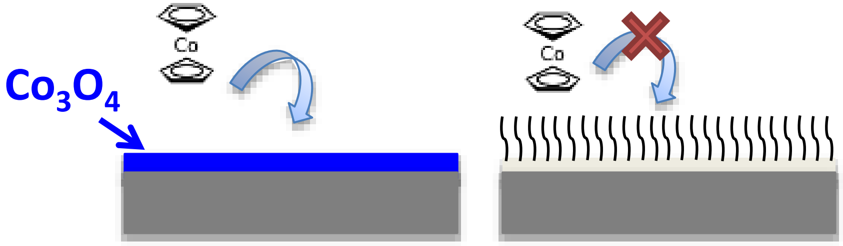
$CH_3(CH_2)_{16}CH_2\text{-}SH$



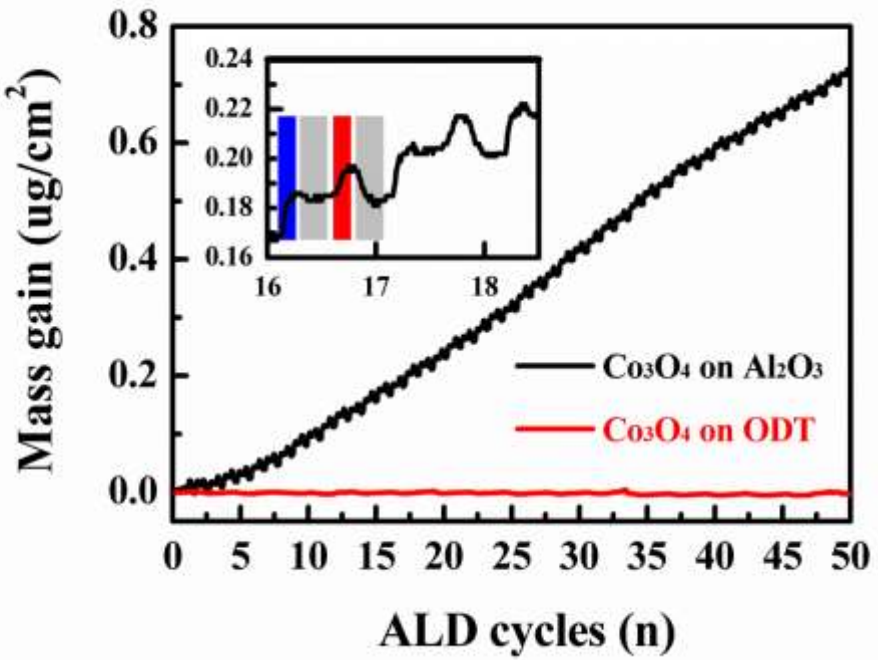
Pt-Al_2O_3 Al$_2$O$_3$



Co_3O_4 ALD growth



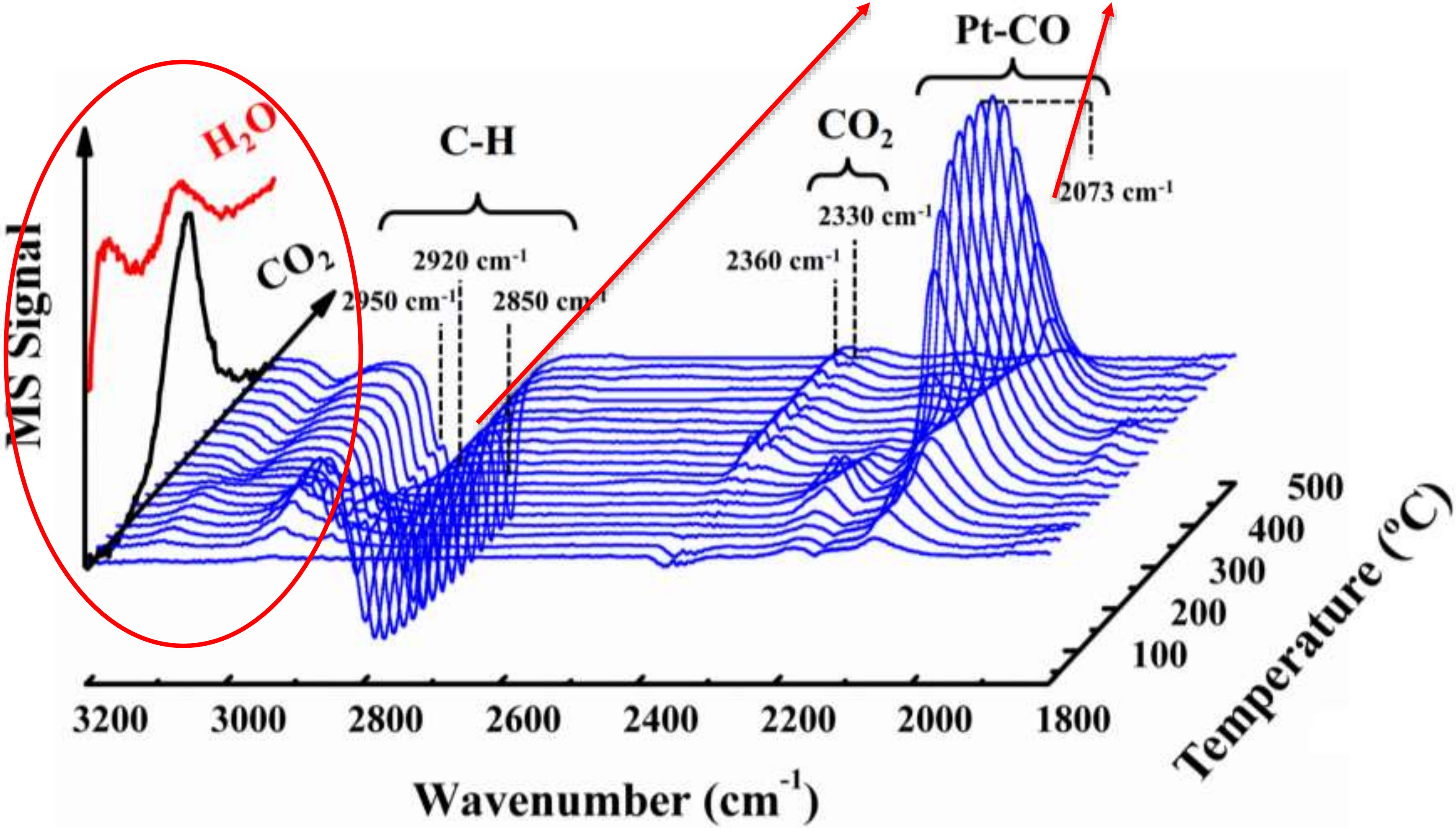
Al_2O_3 ODT/Pt-Al_2O_3



ODT Removal

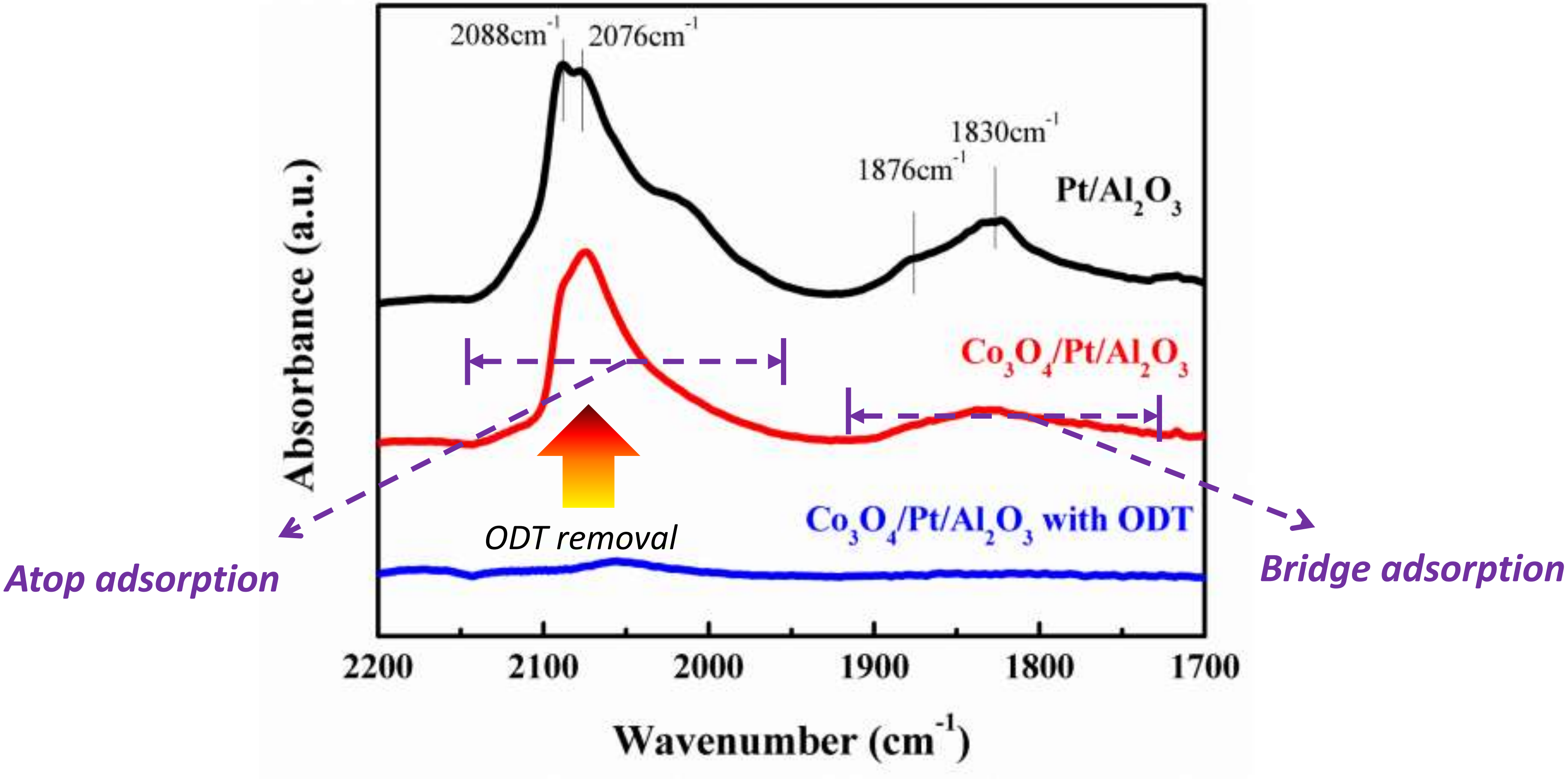
In situ mass spectrometry monitoring signals of CO_2 and H_2O

In situ DRIFTS detecting the stretching bands in C-H and Pt-CO regions



- heating up under oxidative environment with in-situ characterizations

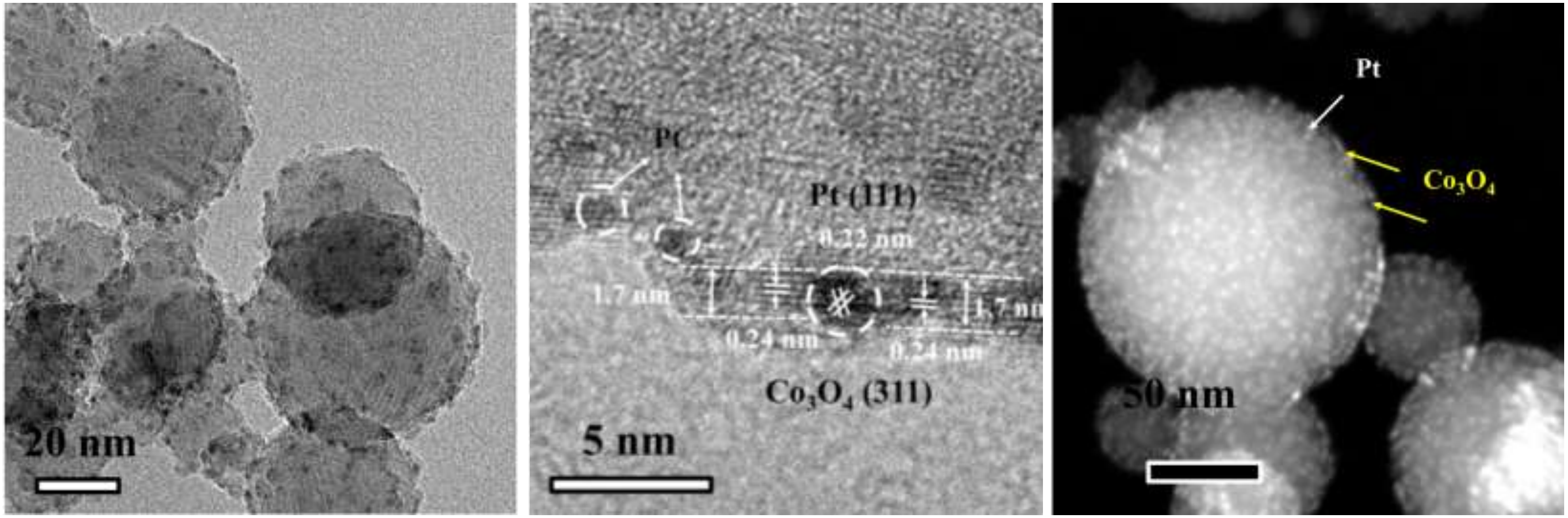
DRIFTS spectra of CO adsorption (RT)

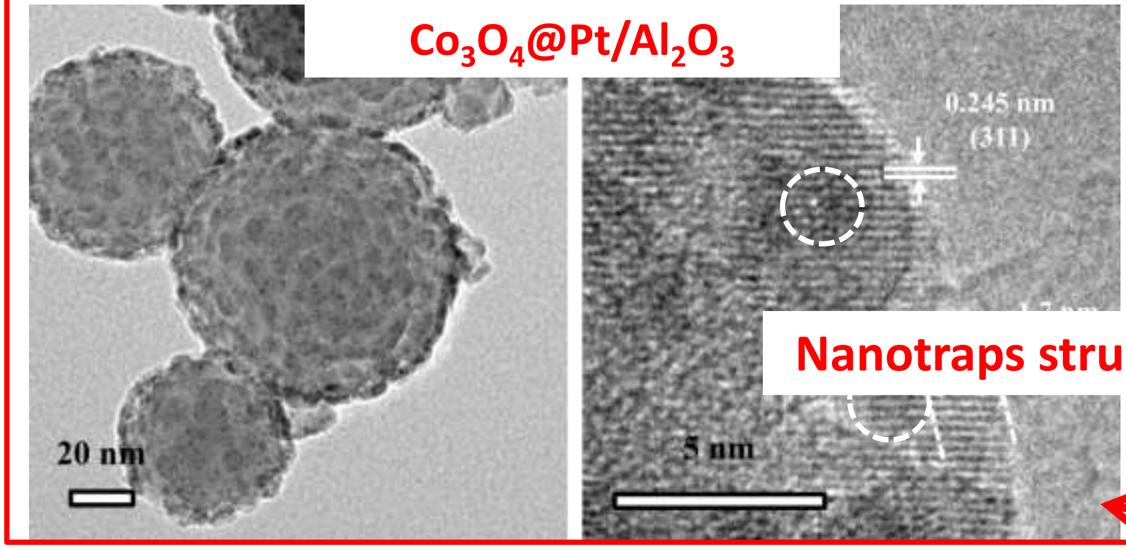


- The blocked adsorption sites on Pt nanoparticles for CO molecule have been exposed after the removal of ODT overlayer.

TEM images of $Co_3O_4/Pt/Al_2O_3$

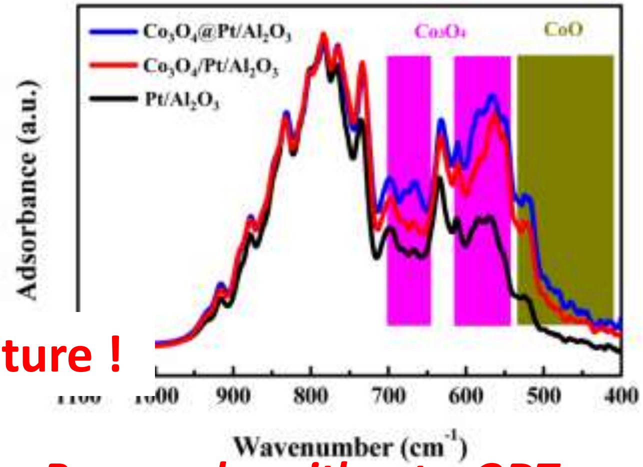
$Co_3O_4/Pt/Al_2O_3$: Pt are inserted into Co_3O_4 nanotraps





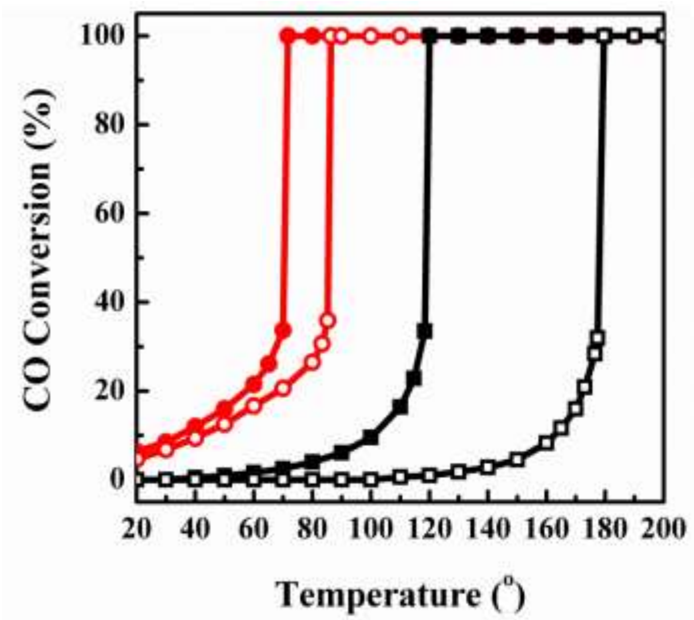
$Co_3O_4@Pt/Al_2O_3$

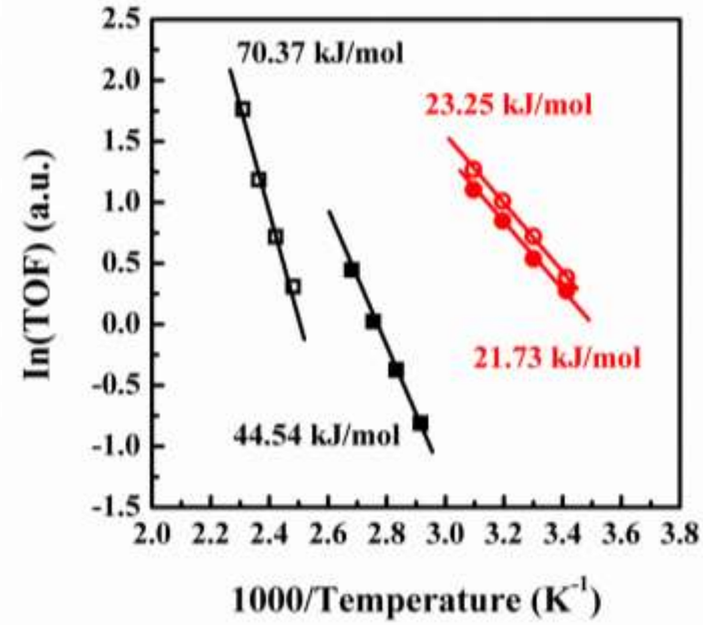
Nanotraps structure !



Prepared without ODT pretreatment

CO oxidation performance

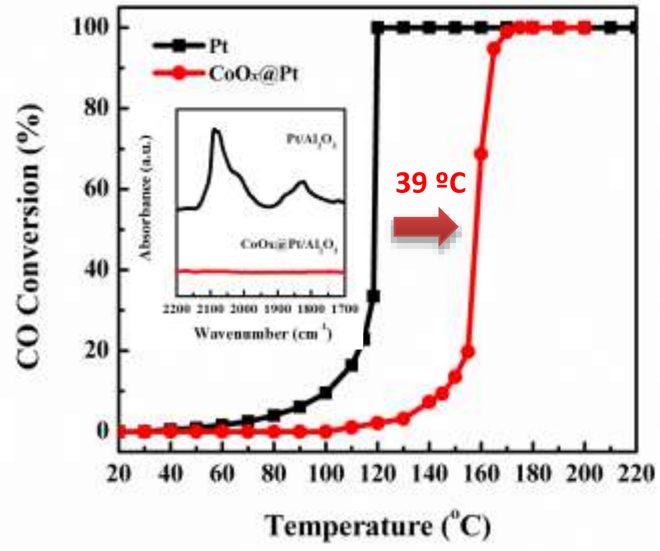




Pt/Al_2O_3 (■), Pt/Al_2O_3-600 (□),

$Co_3O_4/Pt/Al_2O_3$ (●),

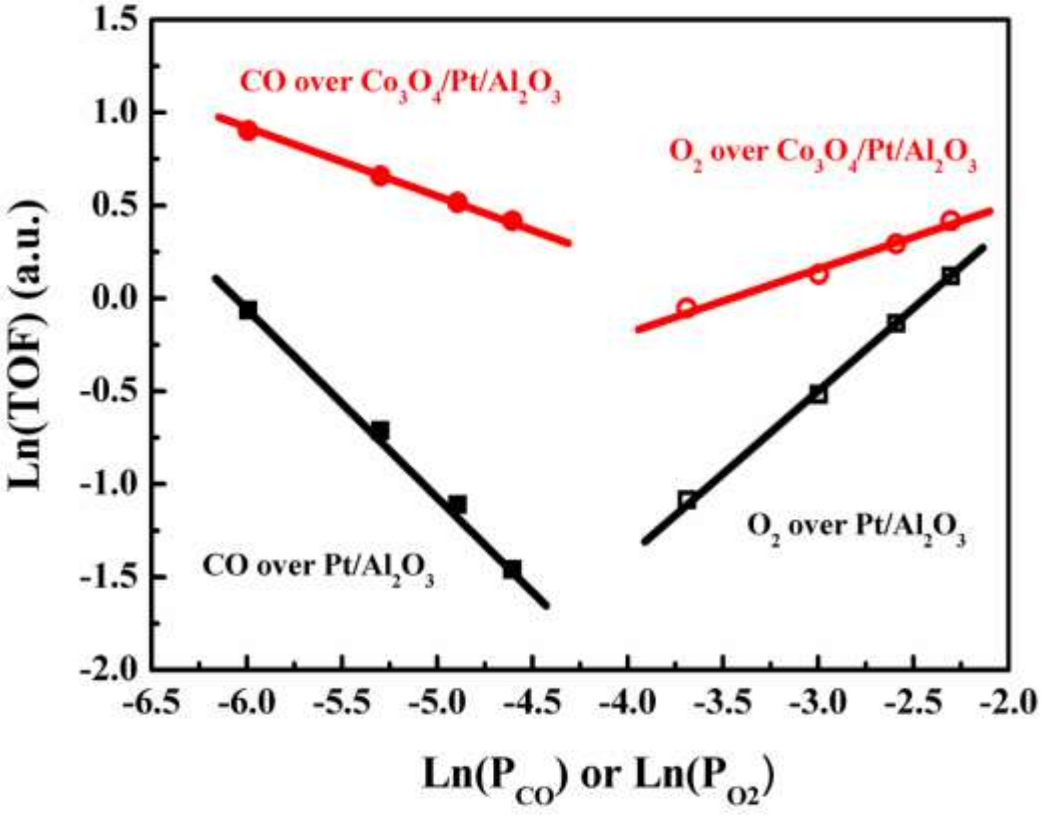
$Co_3O_4/Pt/Al_2O_3$-600 (○)



- $Co_3O_4/Pt/Al_2O_3$ exhibits outstanding low temperature CO oxidation performance, while $Co_3O_4@Pt/Al_2O_3$ shows worse activity than pure Pt/Al_2O_3.

- Co_3O_4 nanotraps can greatly enhance the thermal stability of Pt nanoparticles.

Reaction order



$Co_3O_4/Pt/Al_2O_3$:

$[CO]^{-0.35}[O2]^{0.34}$

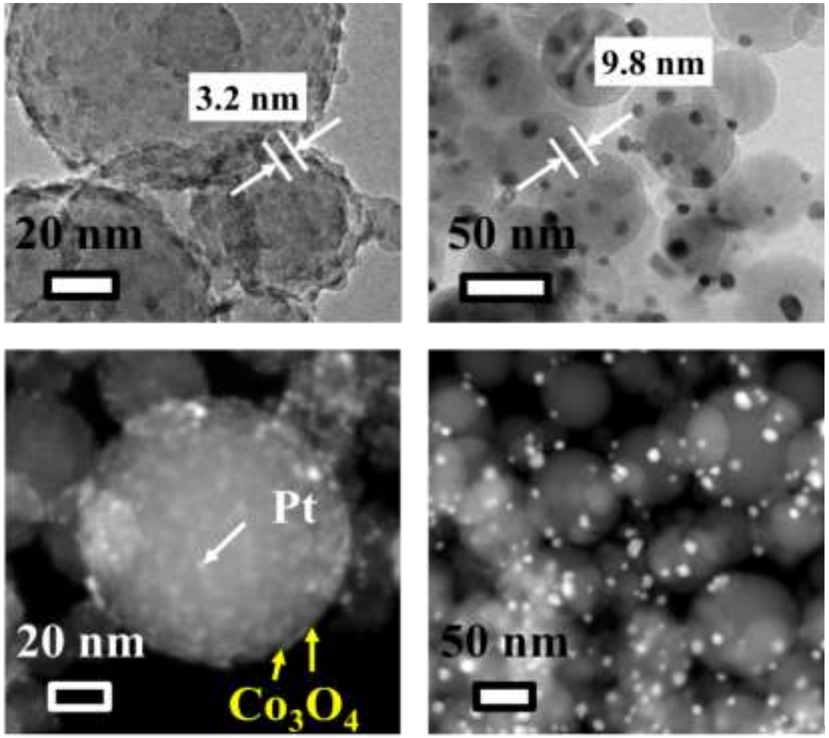
Pt/Al_2O_3:

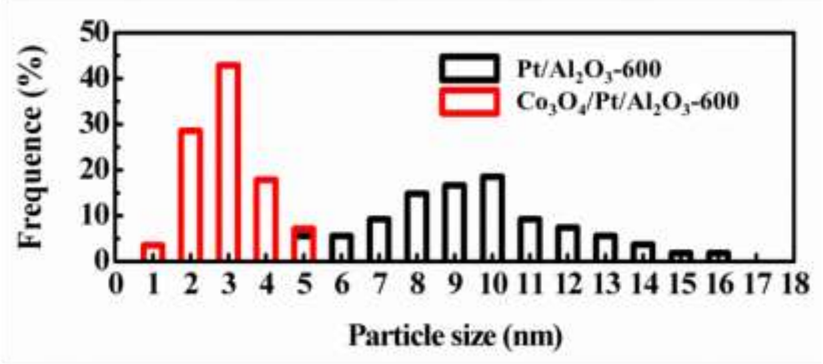
$[CO]^{-0.98}[O_2]^{0.87}$

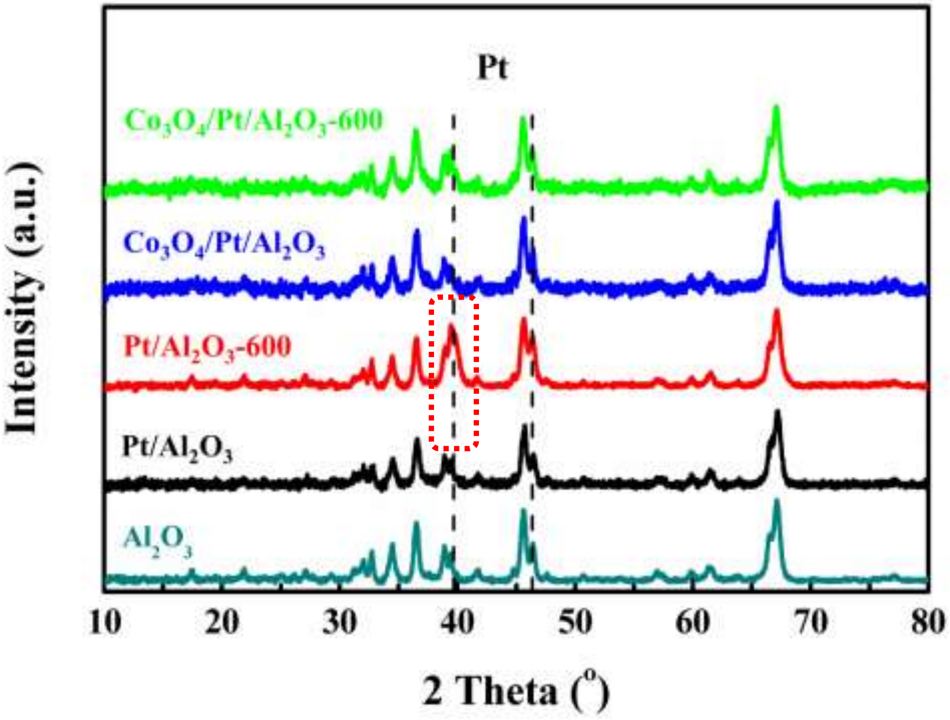
- The larger reaction order of CO and smaller reaction order of O_2 over $Co_3O_4/Pt/Al_2O_3$ indicate the weaker CO adsorption energy and lower O_2 activated barrier, which may due to the strong interfacial interaction between Co_3O_4 and Pt.

Characterizations of calcined catalysts

$Co_3O_4/Pt/Al_2O_3$-600 Pt/Al_2O_3-600



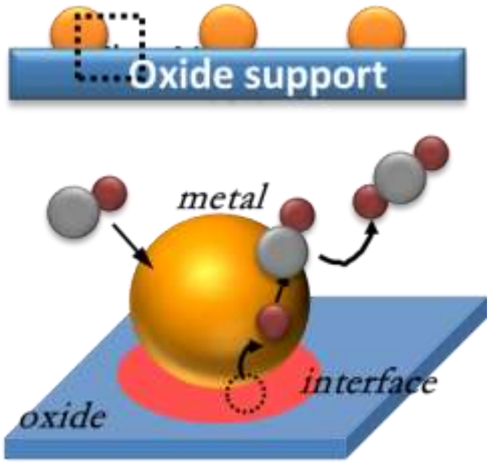




- XRD: Sintering causes Pt crystal size increasing.
- TEM: Pt nanoparticles have been stabilized with Co_3O_4 nanotraps.

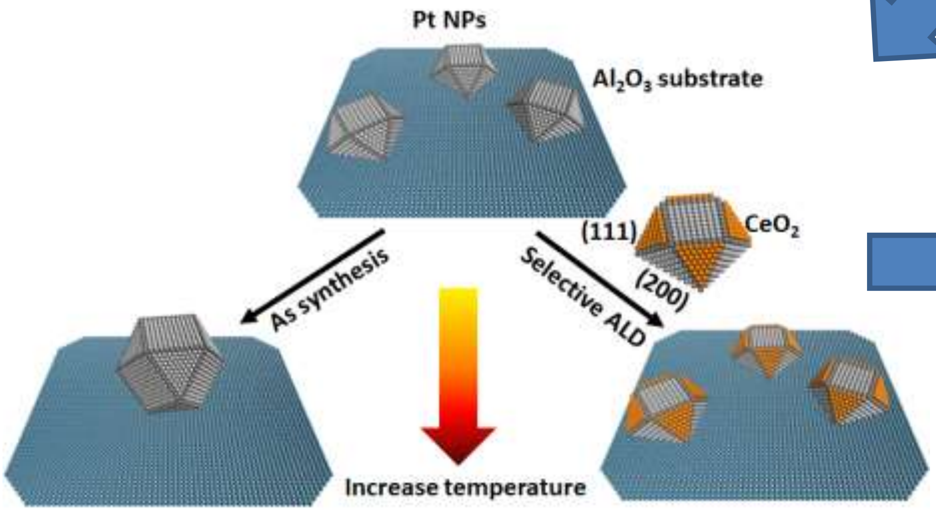
Angew. Chem. Int. Ed. 2017, 56, 1648 –1652

Oxide nanofence coating from facet-selective ALD



supported metal NPs

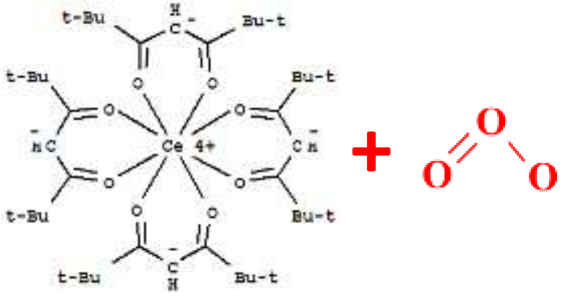
Discontinuous coating



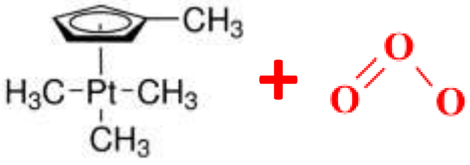
Facet selective ALD

- √ Nanofence barrier cage
- √ Pt-O-Ce strong anchoring
- √ Synergetic effect
- √ Facet edge
- √ Stable in redox environment

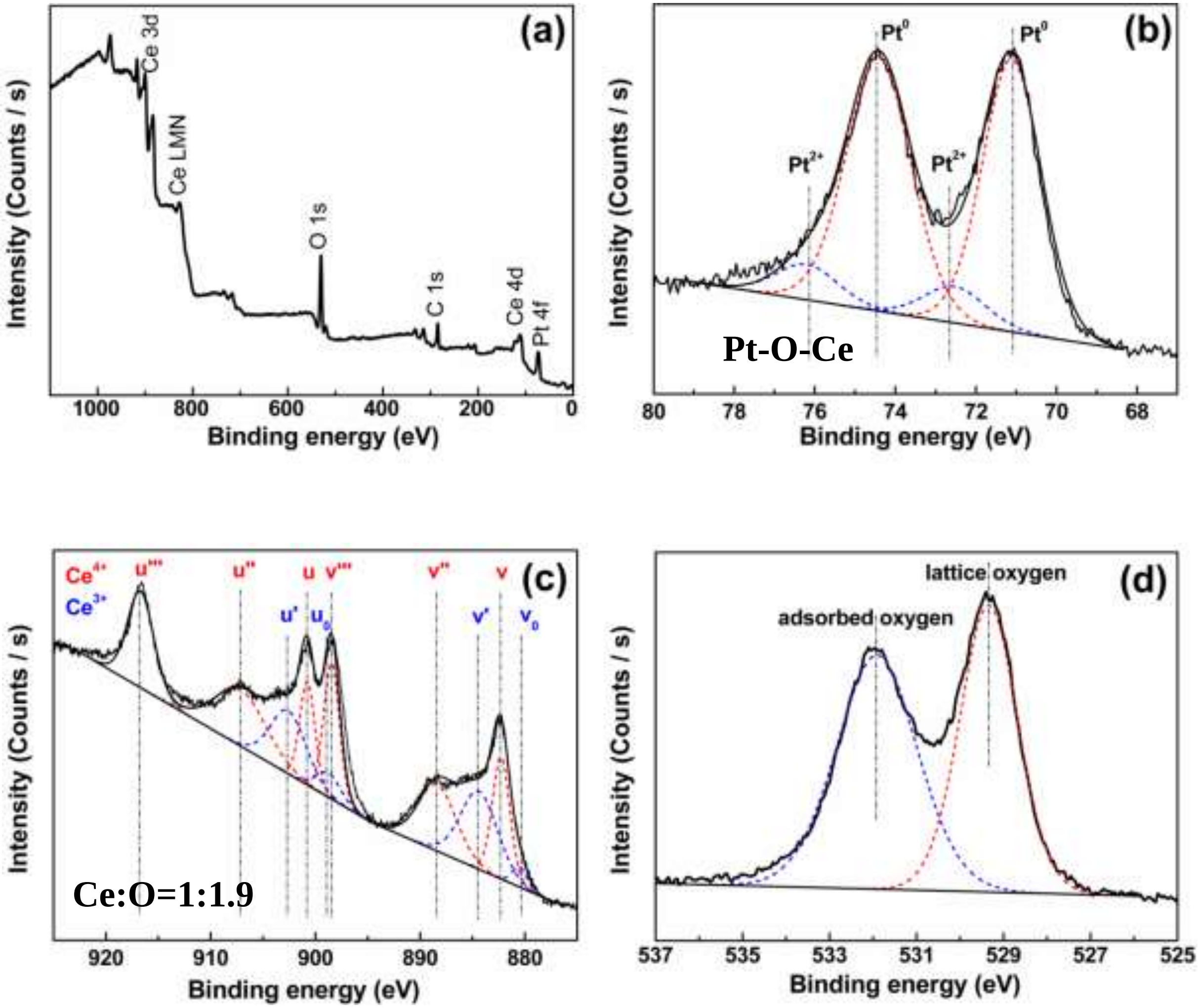
ALD process and XPS of CeO_2 coated Pt



200 º C\160 º C



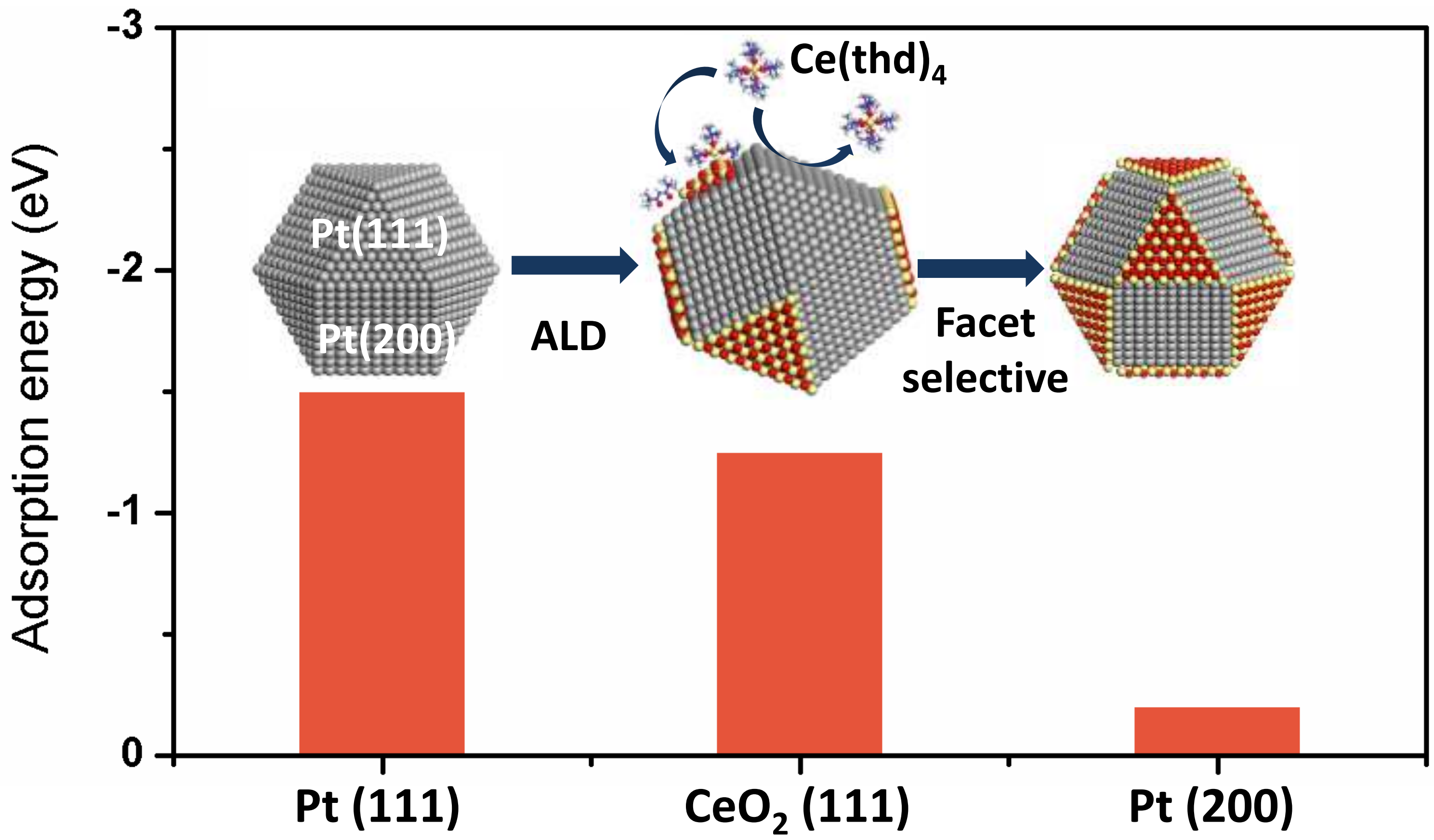
300 º C\65 º C



Pt-O-Ce

Ce:O=1:1.9

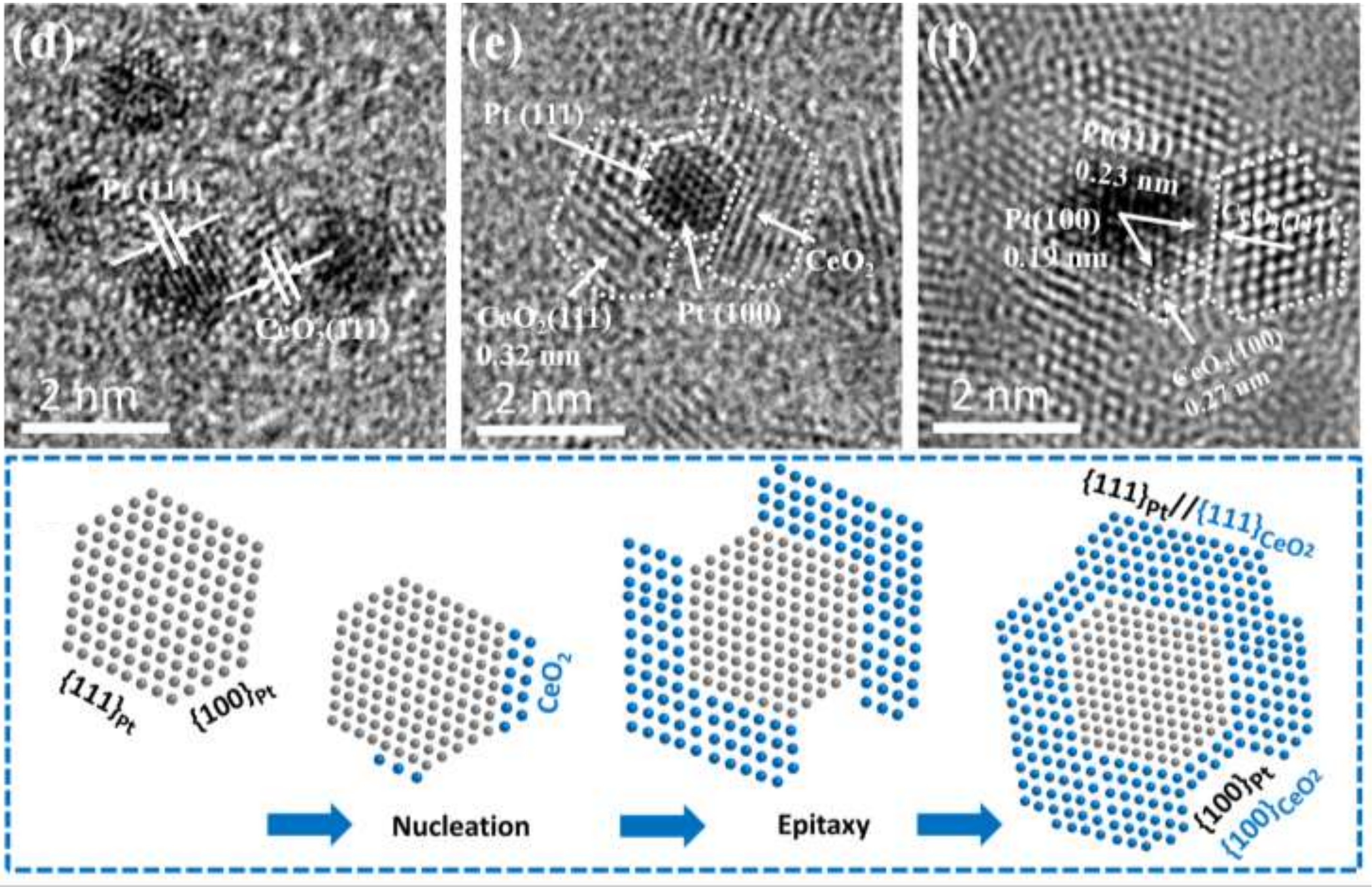
Selective ALD method



- Ce(thd)$_4$ precursor preferentially adsorb on Pt (111) surface via the ligand exchange mechanism.

- After CeO$_2$ has formed on Pt (111), epitaxial growth of CeO$_2$ (111) emerged, Ce(thd)$_4$ does not like to adsorb on Pt (200).

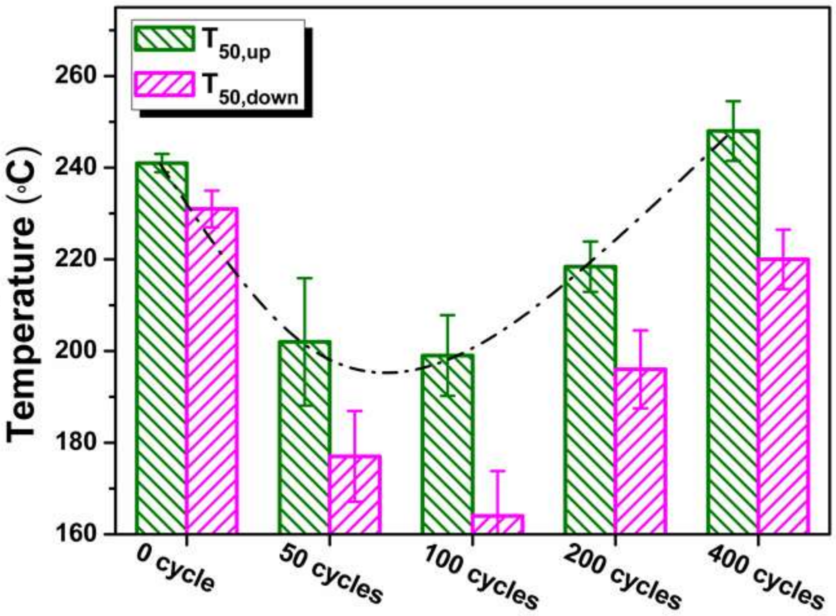
HRTEM Images: Facet Selectivity



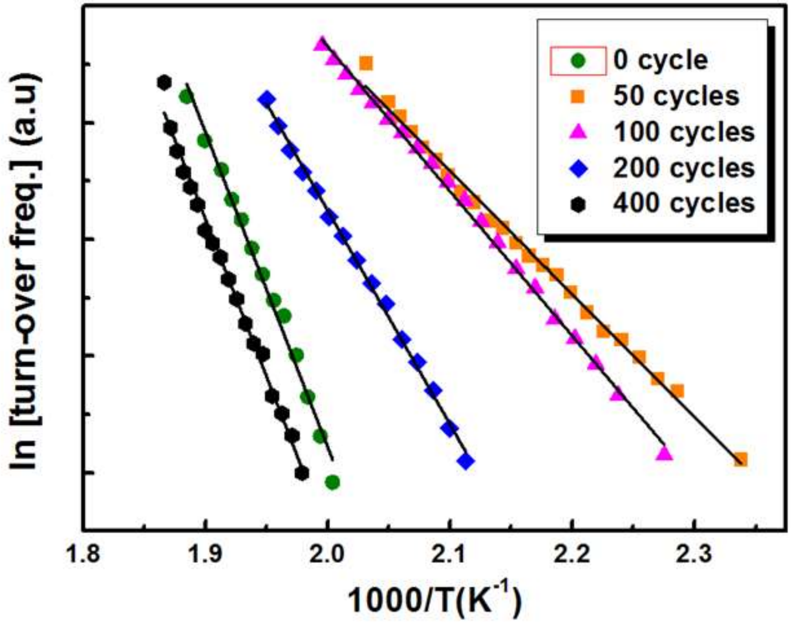
Increasing ALD cycles

- CeO$_2$ are preferred and selected deposited on Pt (111) direction which forming abundant interface.

Catalysts performance test



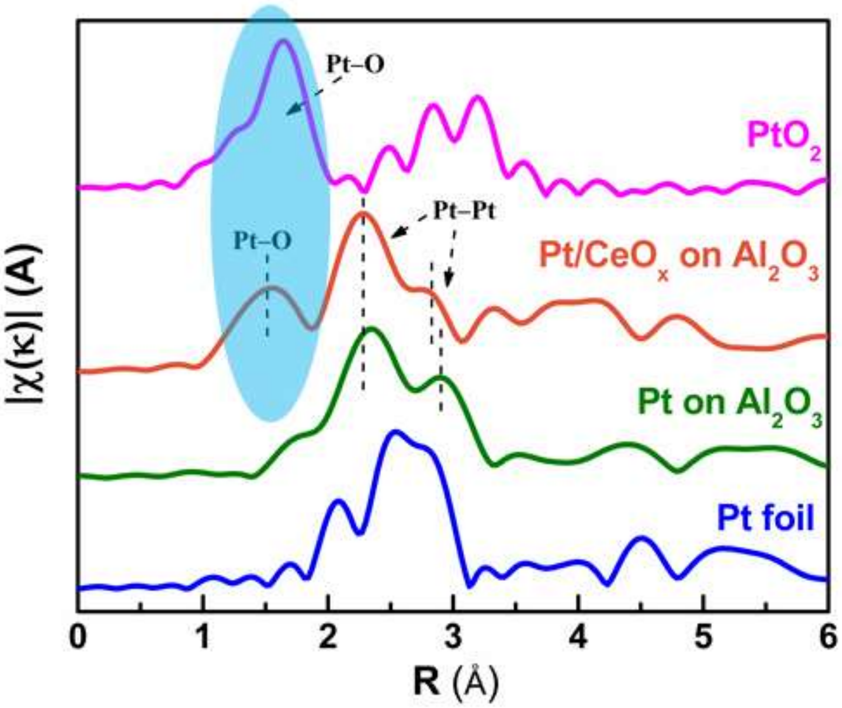
T_{50} vs ALD cycles



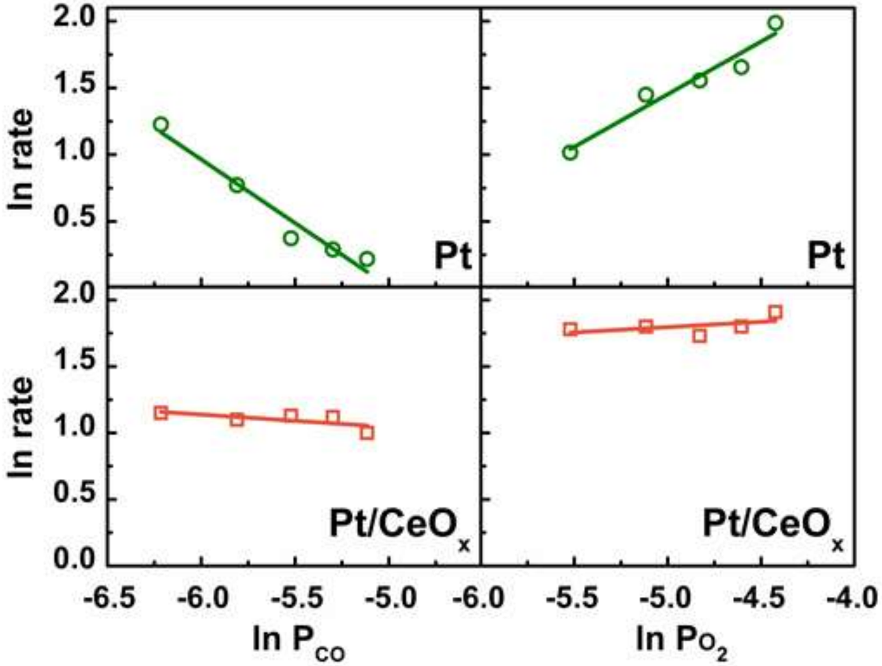
Arrhenius plot of CO conversion

- T_{50},up decrease as CeO_x coating cycles increase within 100 cycles, after optimization coating cycles, the catalytic activity start to decrease
- The activation energy Ea for $CO+O \rightarrow CO_2$ implies the ability of the surface to remove CO during CO oxidation. Ea around 100 cycles has lowest value.

Catalysts performance test



EXAFS spectra at Pt L_3-edge

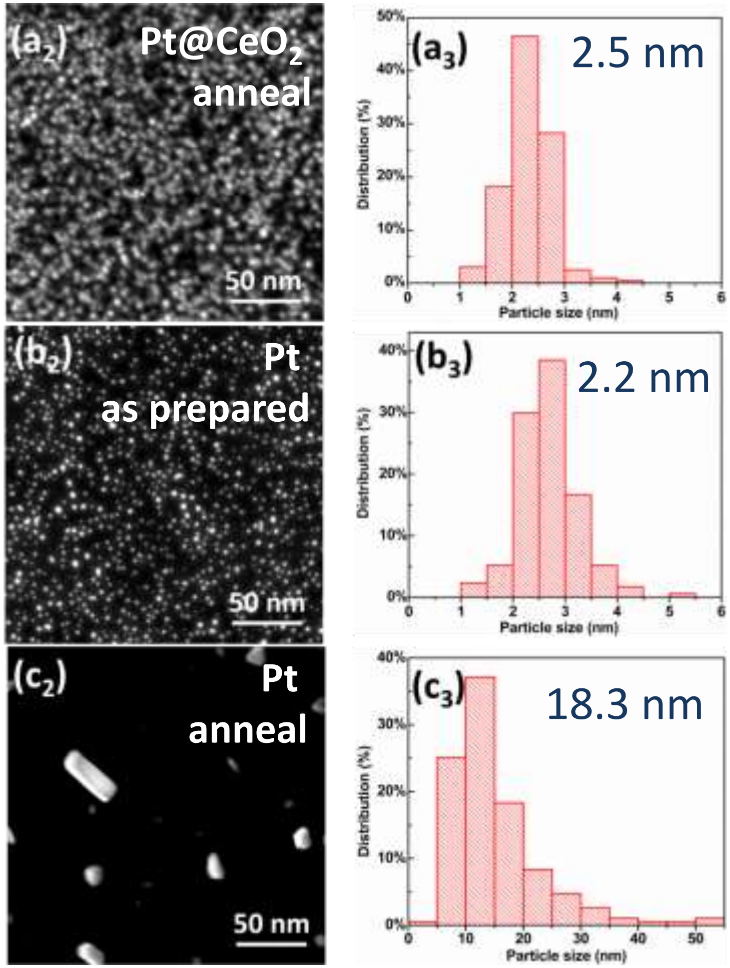


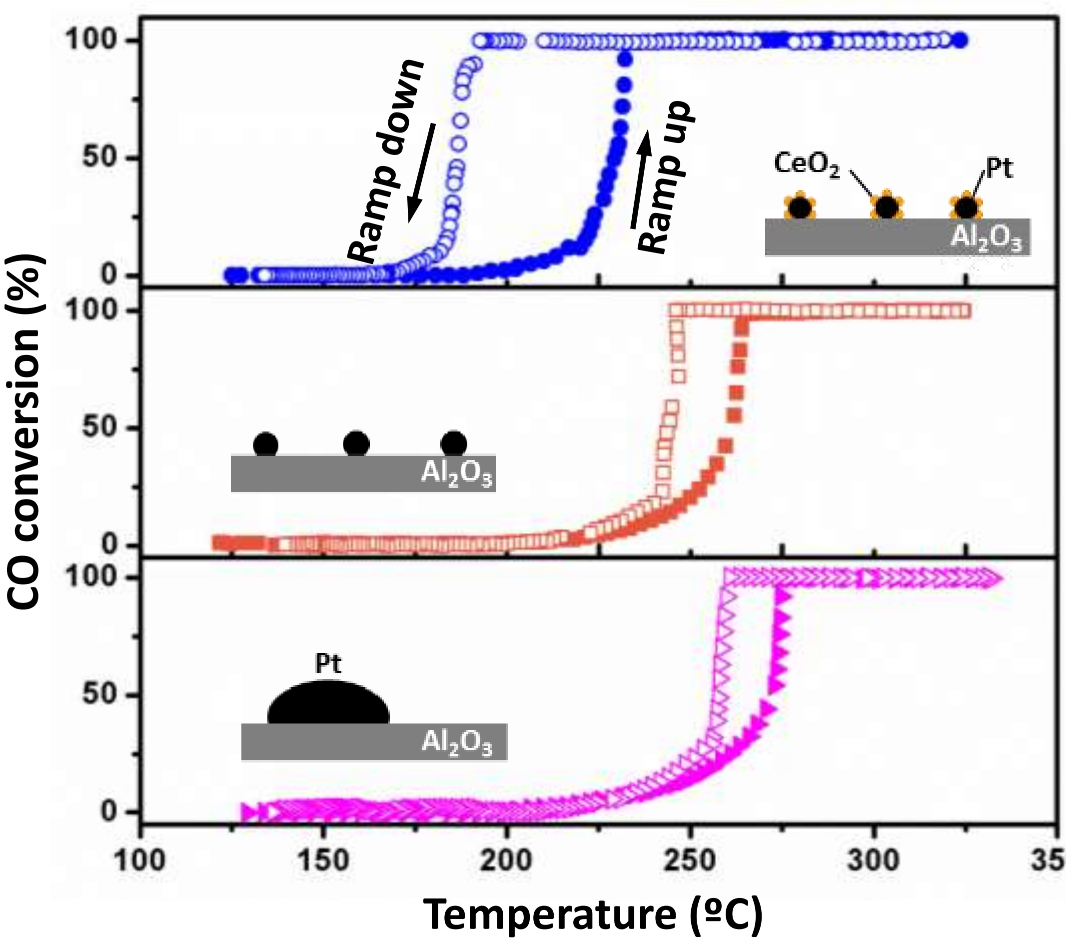
Reaction order test

- Bond length of Pt-Pt in CeO_x coated sample has shifted from 2.73Å to 2.70Å - strong metal oxide interaction effect (SMOI)
- Both CO/O_2 reaction order for Pt/CeO_x is close to 0, indicating the weaker CO adsorption energy and lower O_2 activated barrier

Thermal stability of CeO_2/Pt

With CeO_2 coating layer, the CeO_2/Pt catalysts demonstrate improved thermal stability

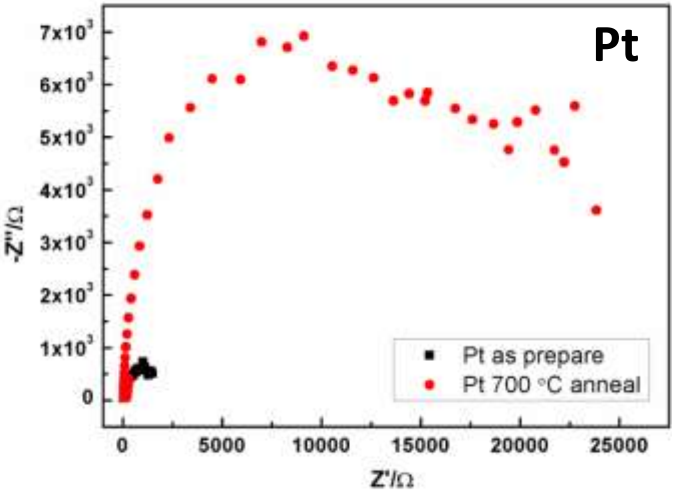


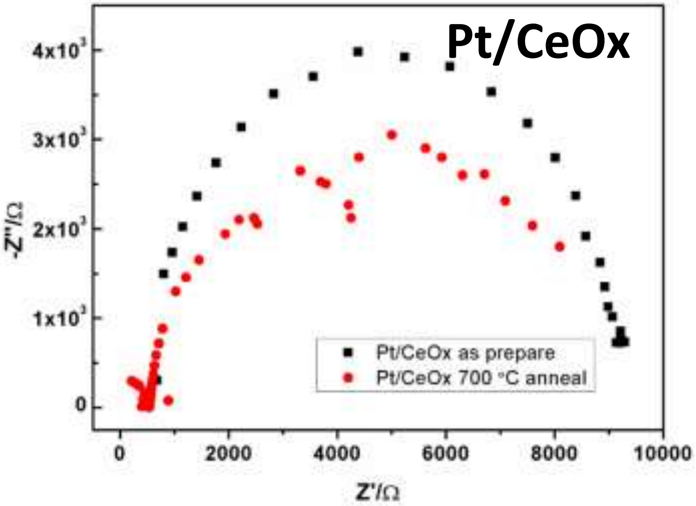


Thermal stability of Pt@CeO_2 catalysts

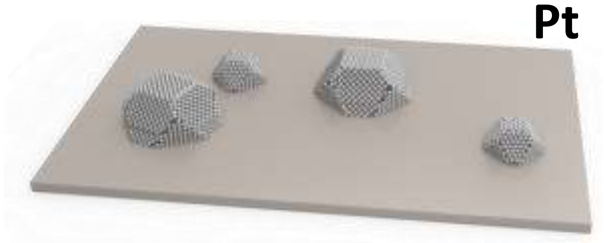
With CeO_2 coating layer, the CeO_2/Pt catalysts demonstrate improved thermal stability

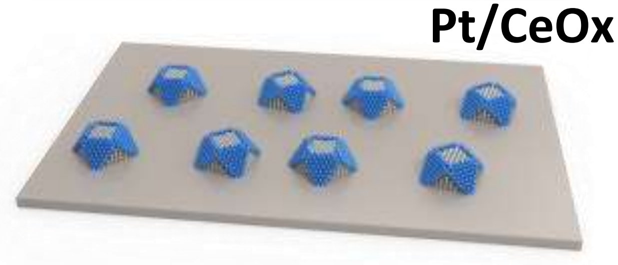
EIS test





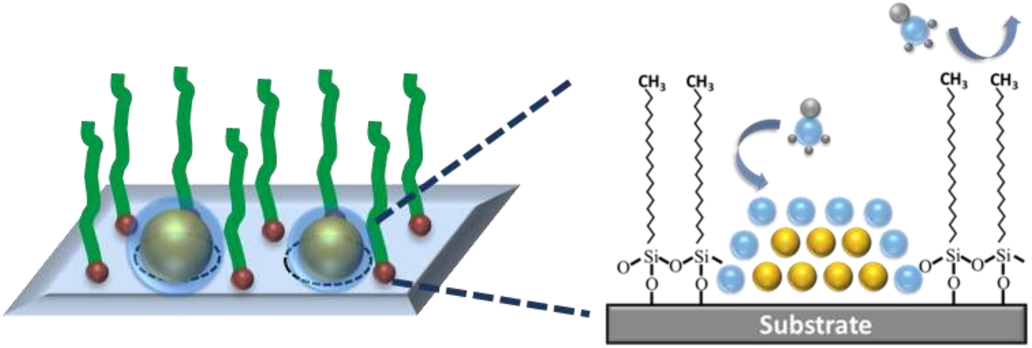
	Pure Pt	50 cyc CeOx	100 cyc CeOx	200 cyc CeOx
fresh	232℃	195℃	188℃	206℃
600℃	245℃	201℃	190℃	207℃
700℃	276℃	206℃	192℃	213℃
750℃	279℃	223℃	219℃	211℃



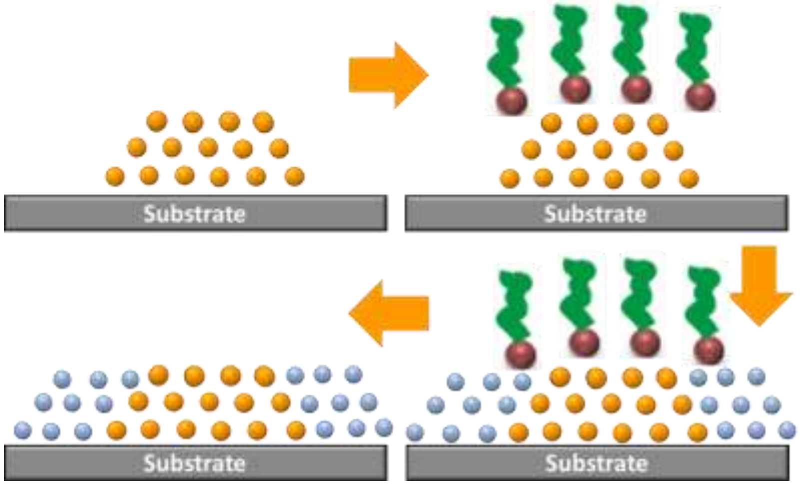


Summary: Selective ALD methods

1. Surface modification with self-assembled monolayers



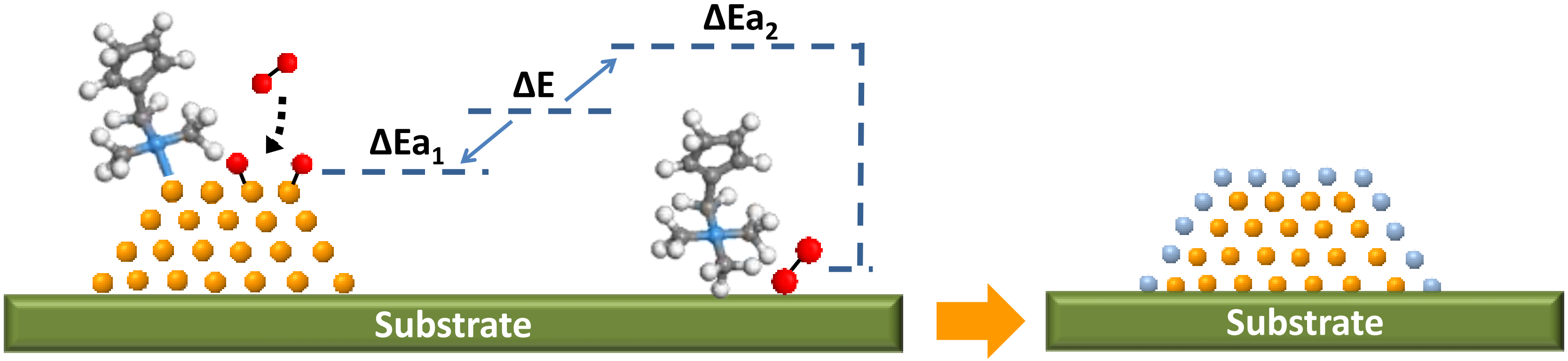
Pd/Pt Core shell nanoparticles



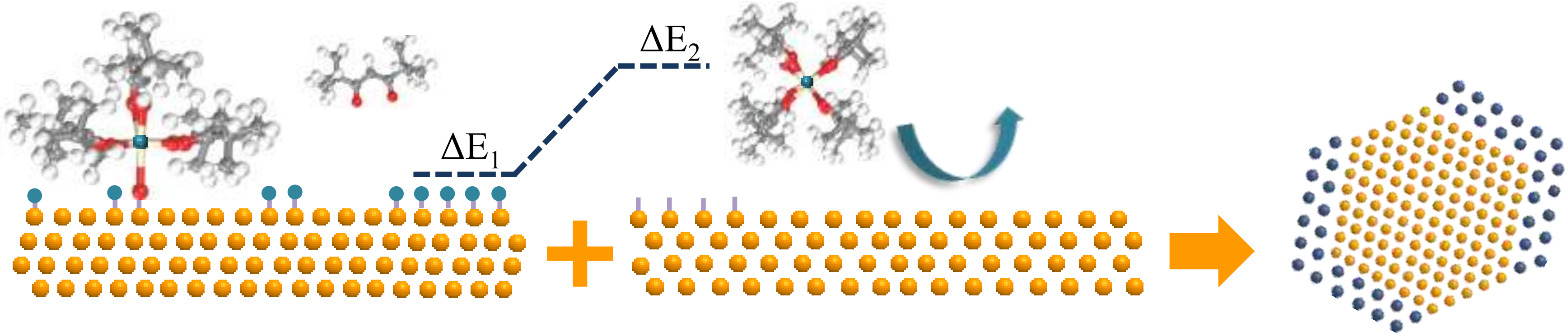
Pt/CoOx Oxide nanotraps

Summary: Selective ALD method

2. Precursor activation energy difference



3. Facet selective ALD-binding energy/lattice constant difference



Summary and Outlook

- Selective ALD is a quite powerful synthesis method to create model catalysis.
- Energy difference between different surfaces to obtain selectivity can be quite subtle.
- Defects can be utilized.

Challenges and Outlooks:

- Tiny structures with enormous surface areas, requires new processes and equipment.
- Bulky ALD precursors with low reactivity for many transition metal oxides, needs better chemicals.
- Surface is not well defined with edges and facets, ideal film theory may not work here.
- Selective deactivation of defects and *in-situ* spectroscopic characterizations required to understand growth mechanism.