The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

2269-5

Workshop on New Materials for Renewable Energy

17 - 21 October 2011

Synthesis of dispersible core-shell metal@oxide materials and their application as stable fuel cell catalysts

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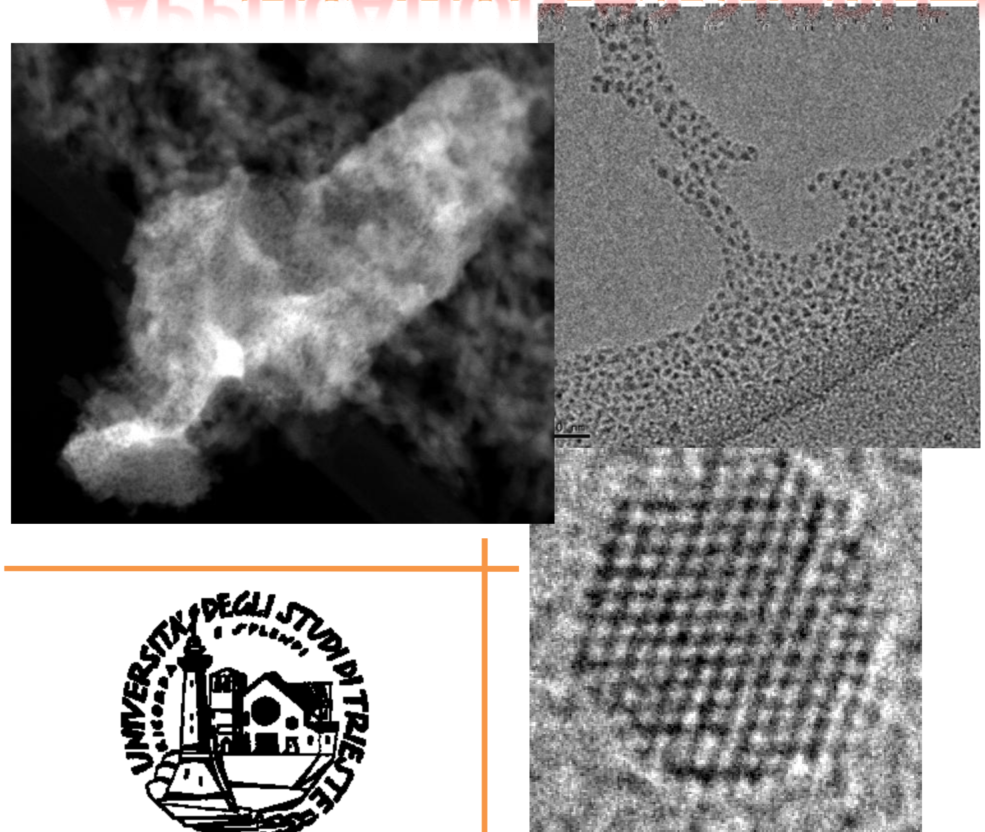
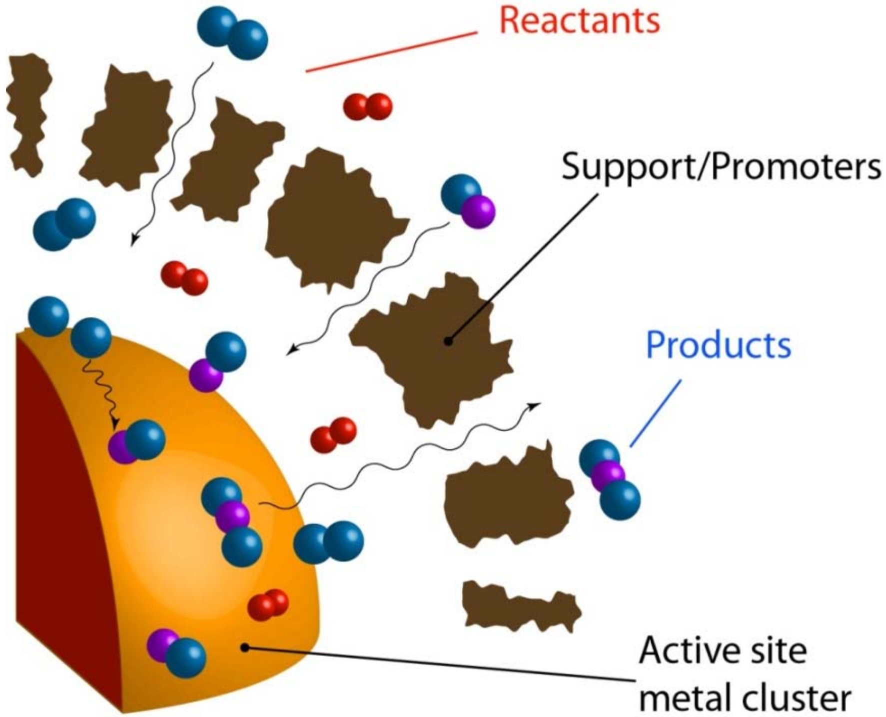
University of Trieste
Italy

SYNTHESIS OF DISPERSIBLE CORE-SHELL METAL@OXIDE MATERIALS AND THEIR APPLICATION AS STABLE FUEL CELL CATALYSTS





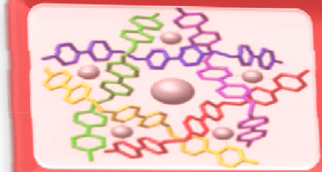
MATTEO CARGNELLO

R. J. GORTE, P. FORNASIERO

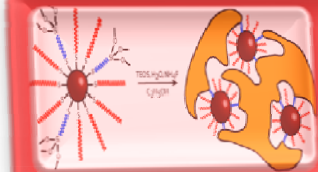
WORKSHOP ON NEW MATERIALS FOR ENERGY

ICTP-SISSA, TRIESTE, October 18th 2011

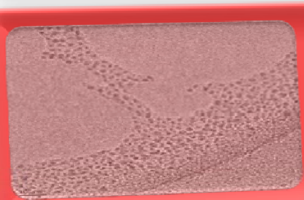
OUTLINE



INTRODUCTION



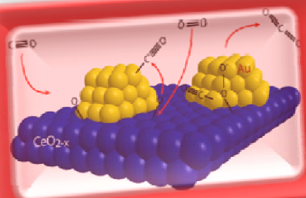
DESIGN OF METAL@OXIDE ARCHITECTURES



DISPERSIBLE Pd@CeO_2 STRUCTURES

Synthesis and characterization

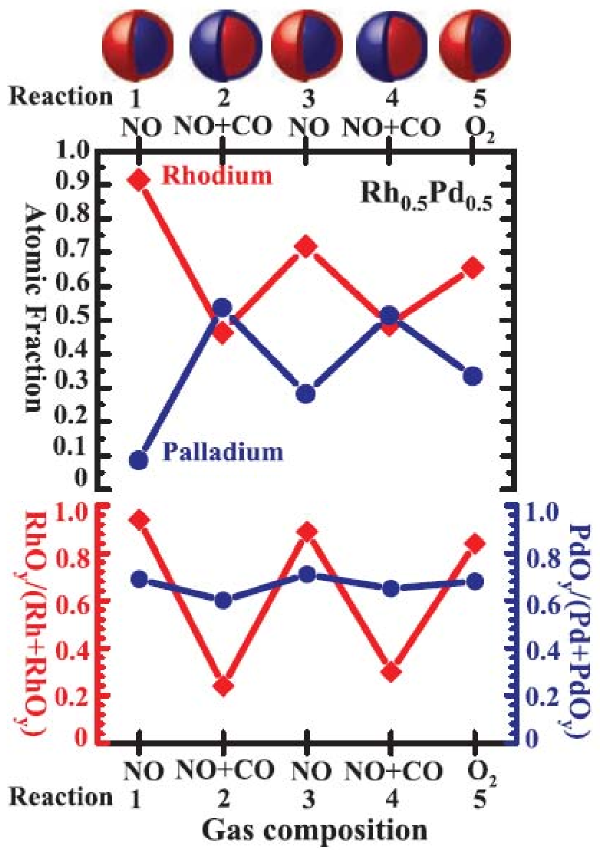
Pd@CeO_2 AS FUEL CELL CATALYSTS

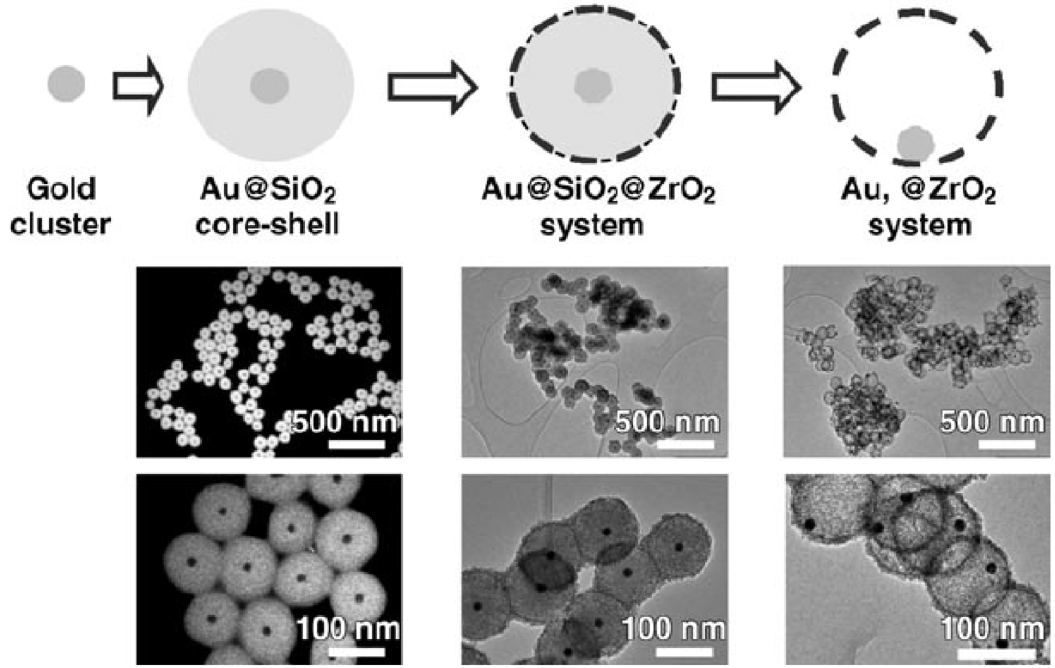


CONCLUSIONS

INTRODUCTION: CORE-SHELL STRUCTURES

Tuneable properties different than constituent single counterparts





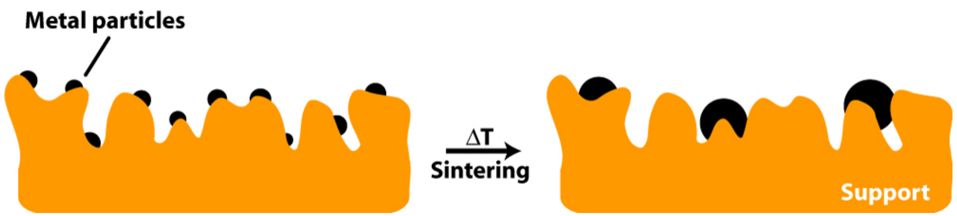
Nanometer control over the nanostructure

Arnal, P. *et al*. Angew. Chem. Int. Ed. 2006, *45*, 8224

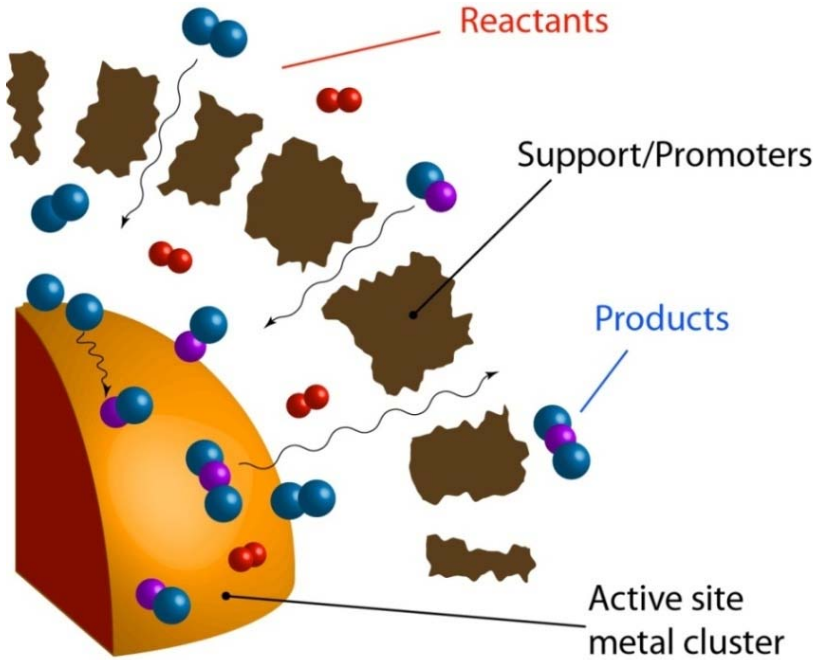
Reaction-driven reconstruction

Tao, F. *et al*. Science 2008, *322*, 932

CORE-SHELL STRUCTURES: MOTIVATIONS IN CATALYSIS



Sintering due to thermal treatments decreases the catalytic activity



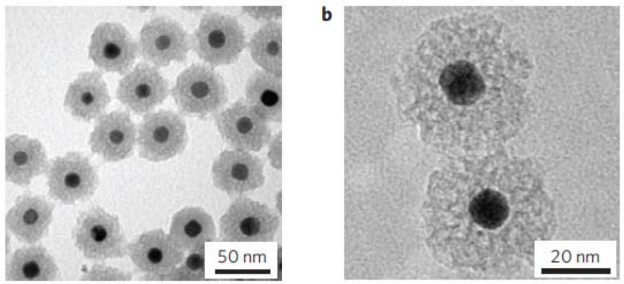
"EMBEDDING APPROACH"

Encapsulation of preformed metal nanoparticles in the support to limit sintering and obtain new properties

Chapter 2 in "Nanorods, Nanotubes and Nanomaterials Research Progress", Nova Science Publishers, 2008

ChemSusChem 2010, *3*, 24-42

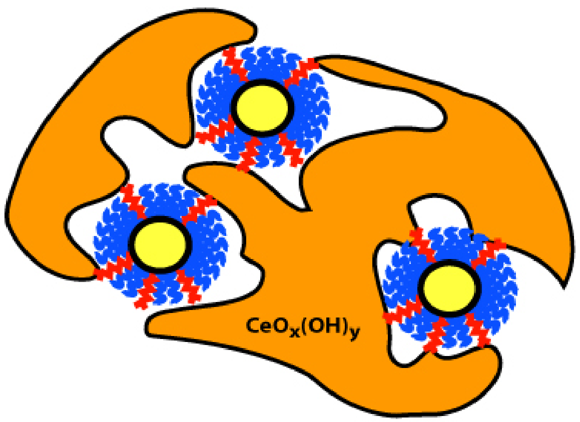
CORE-SHELL STRUCTURES IN CATALYSIS: MAIN PROBLEM #1



$Pt@SiO_2$
Joo, S. H. *et al.*
Nature Mater.
2009, *8*, 126

An “inert” support in catalysis!

CeO_2



$Au@CeO_2$ for PROX

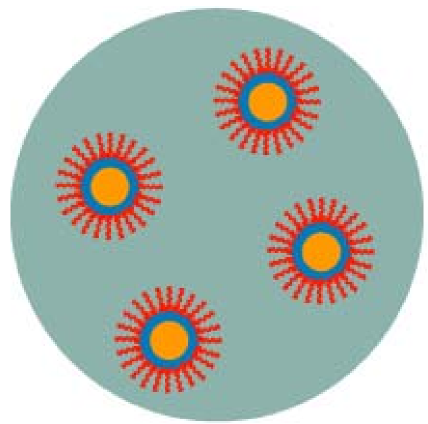
Chem. Mater. **2010**, *22*, 4335

ZrO_2

Ru@LSZ for NH_3 decomposition

ChemCatChem **2011**, *2*, 1096

TiO_2

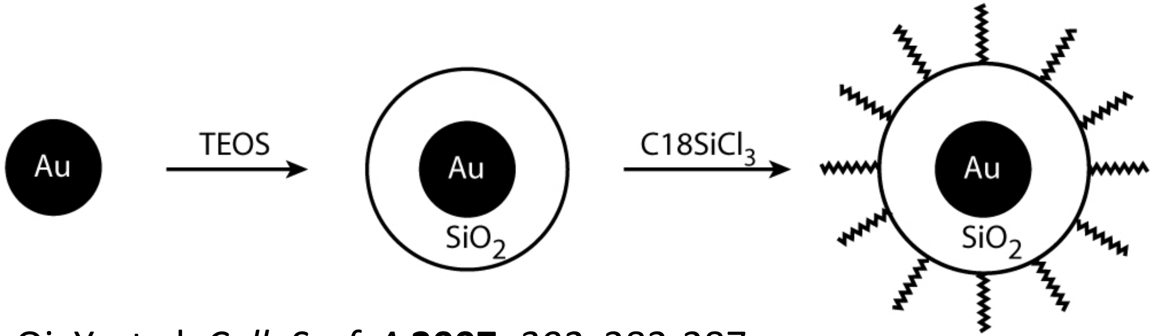


$Cu@TiO_2$ for photocatalysis

J. Phys. Chem. A **2010**, *114*, 3916

CORE-SHELL STRUCTURES IN CATALYSIS: MAIN PROBLEM #2

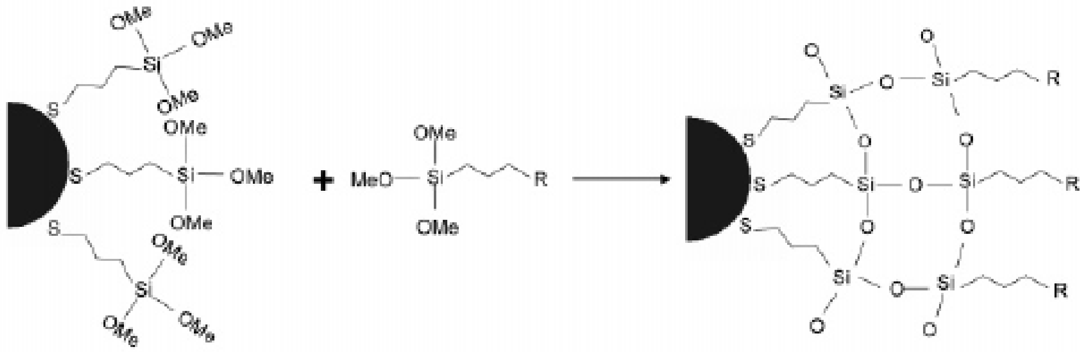
Dispersibility is an issue!
Agglomeration not desired



Qi, Y. et al. *Coll. Surf. A* **2007**, *302*, 383-387

Grafitization of hydrocarbon chains on the surface of SiO_2

Direct synthesis of nanoparticles containing linker silanes

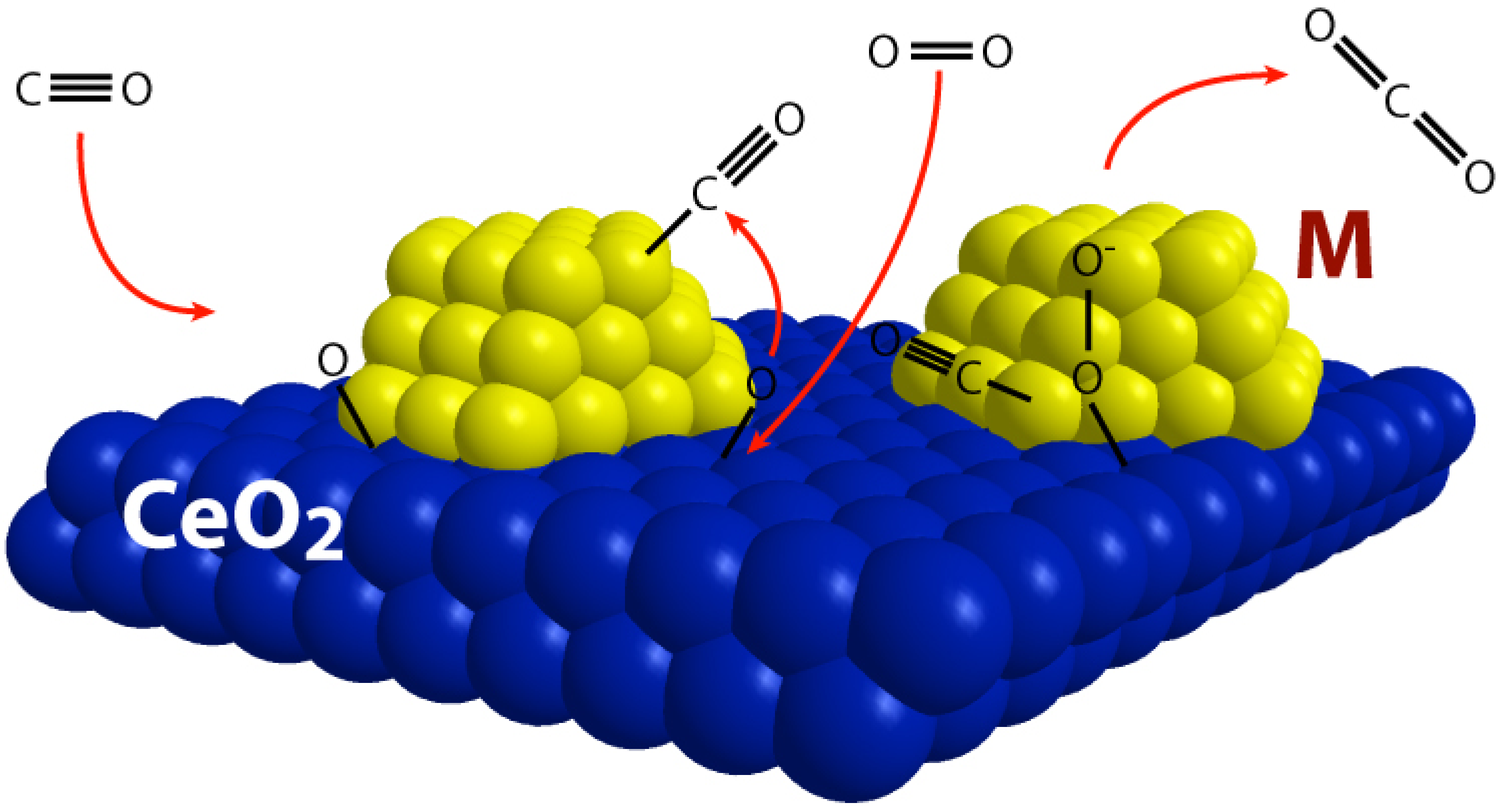


R: $NHCH_2CH_2NH_2$, $PO_3(Me)$, PEG.

Jana, N. R. et al. *Chem. Mater.* **2007**, *19*, 5074-5082

CORE-SHELL STRUCTURES IN CATALYSIS: METAL – OXIDE INTERFACES

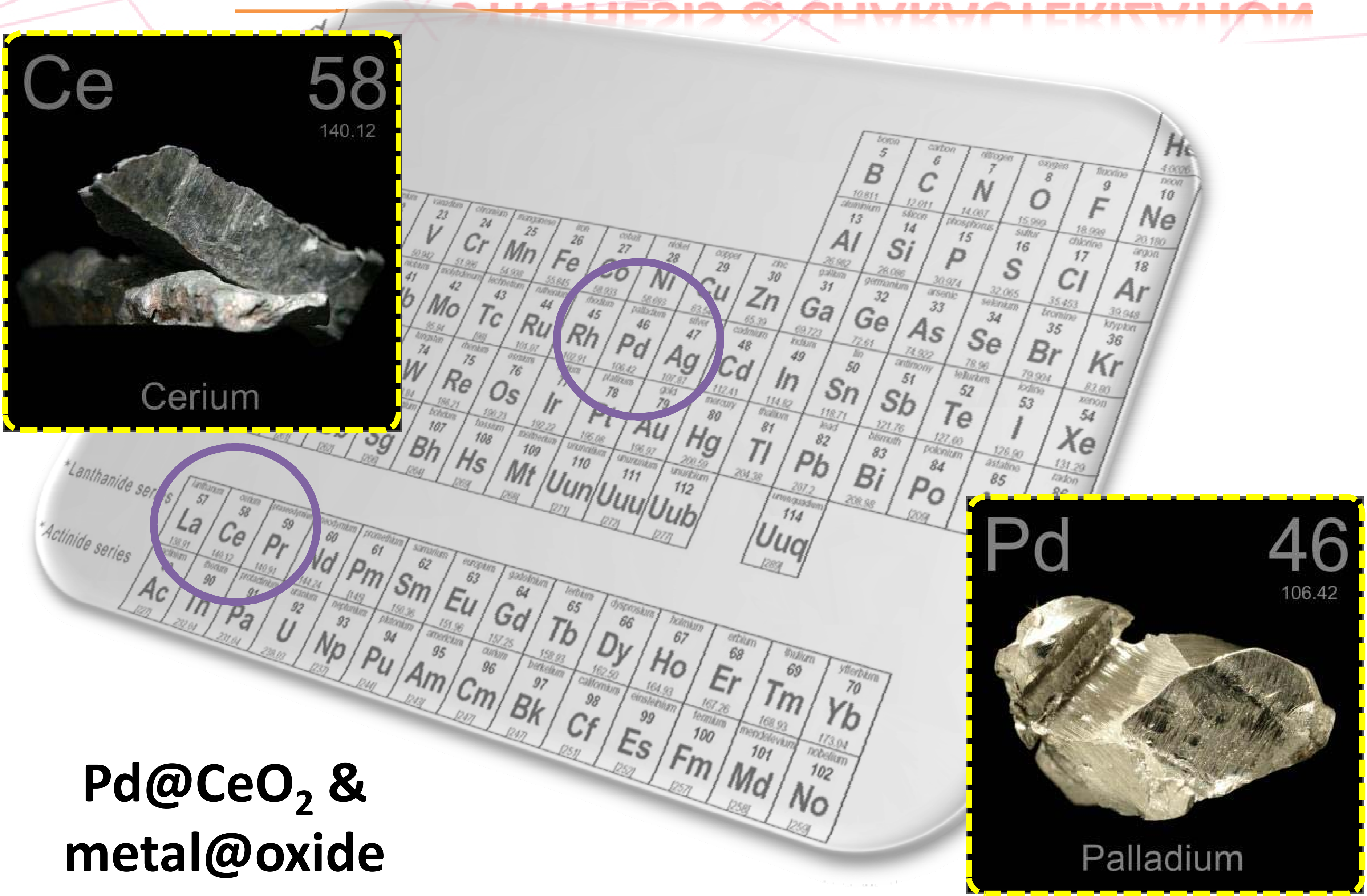
High activity:
- low metal loadings
- low operative temperatures



cooperative effect!

Guzman, B. C. et al. *Angew. Chem. Int. Ed.* **2005**, *44*, 4778

CORE-SHELL STRUCTURES
SYNTHESIS & CHARACTERIZATION

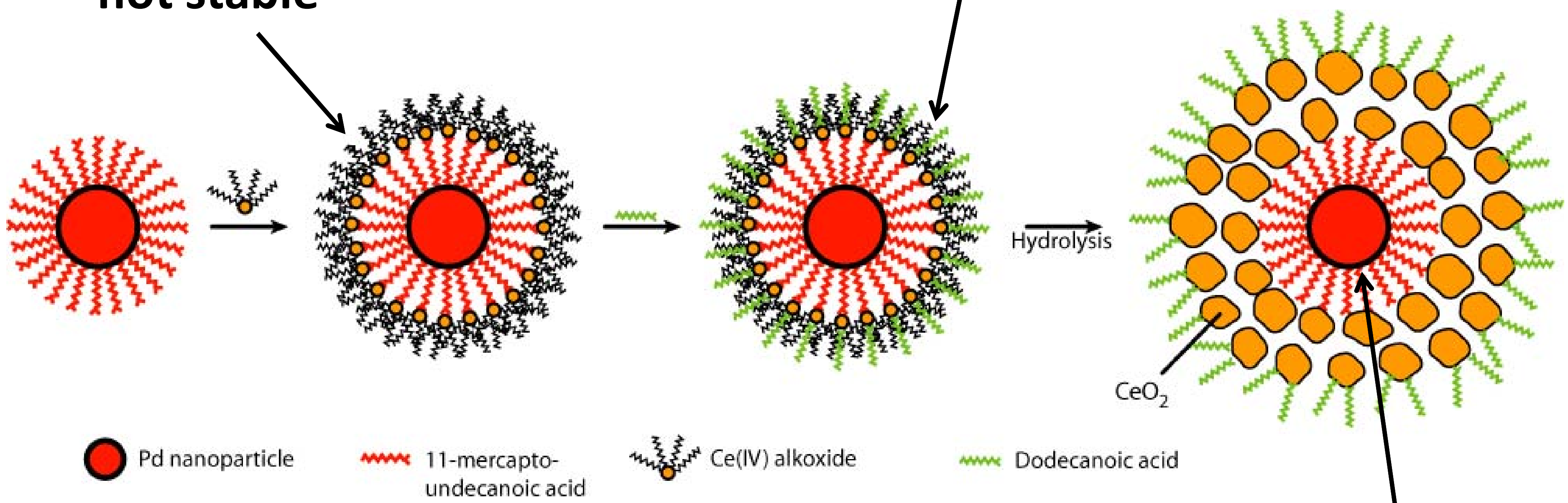


Pd@CeO$_2$ &
metal@oxide

CORE-SHELL STRUCTURE DESIGN

Ce-OR bond
not stable

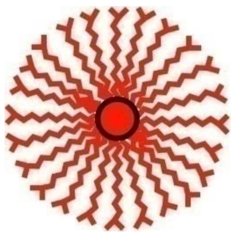
COOH-Ce bond
stable



Pd-S bond
stable

Possibility to tune both core and shell compositions!

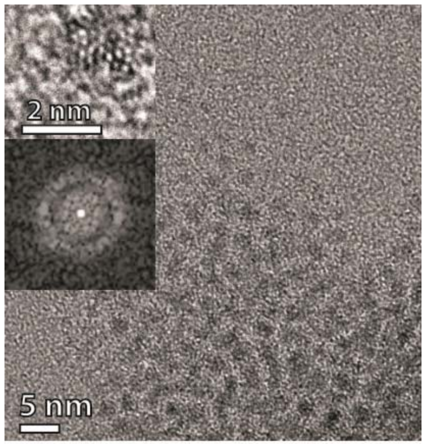
ASSEMBLY OF DISPERSIBLE Pd@CeO_2 SYSTEMS

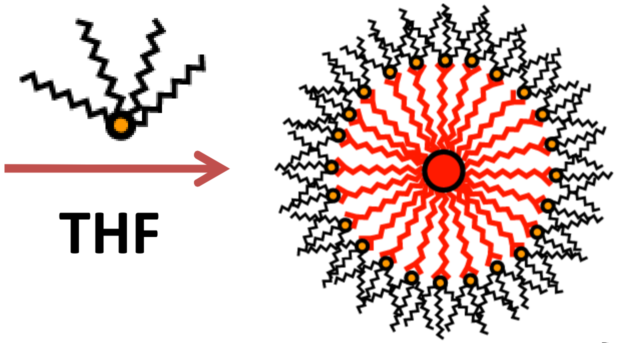


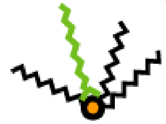
MUA-Pd NPs

MUA: 11-Mercapto Undecanoic Acid

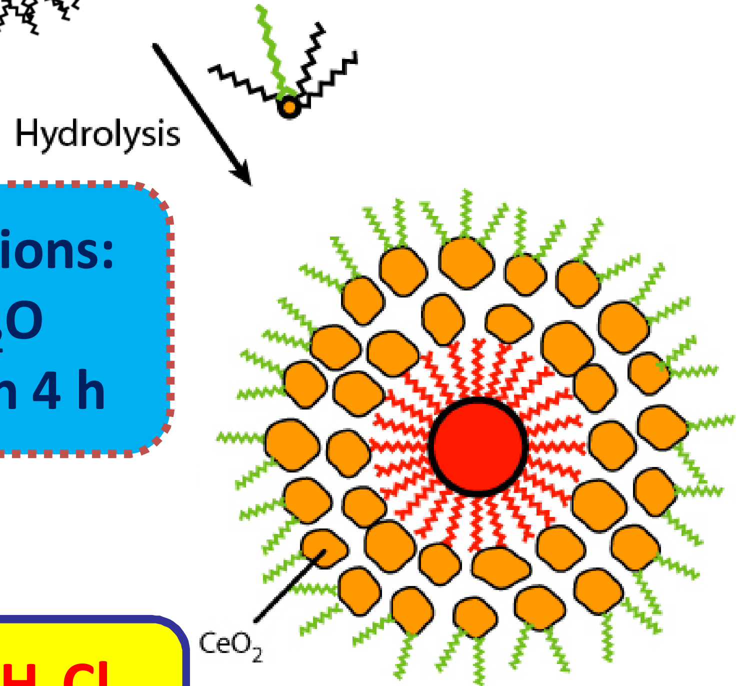
Pd core size: 1.8 ± 0.2 nm







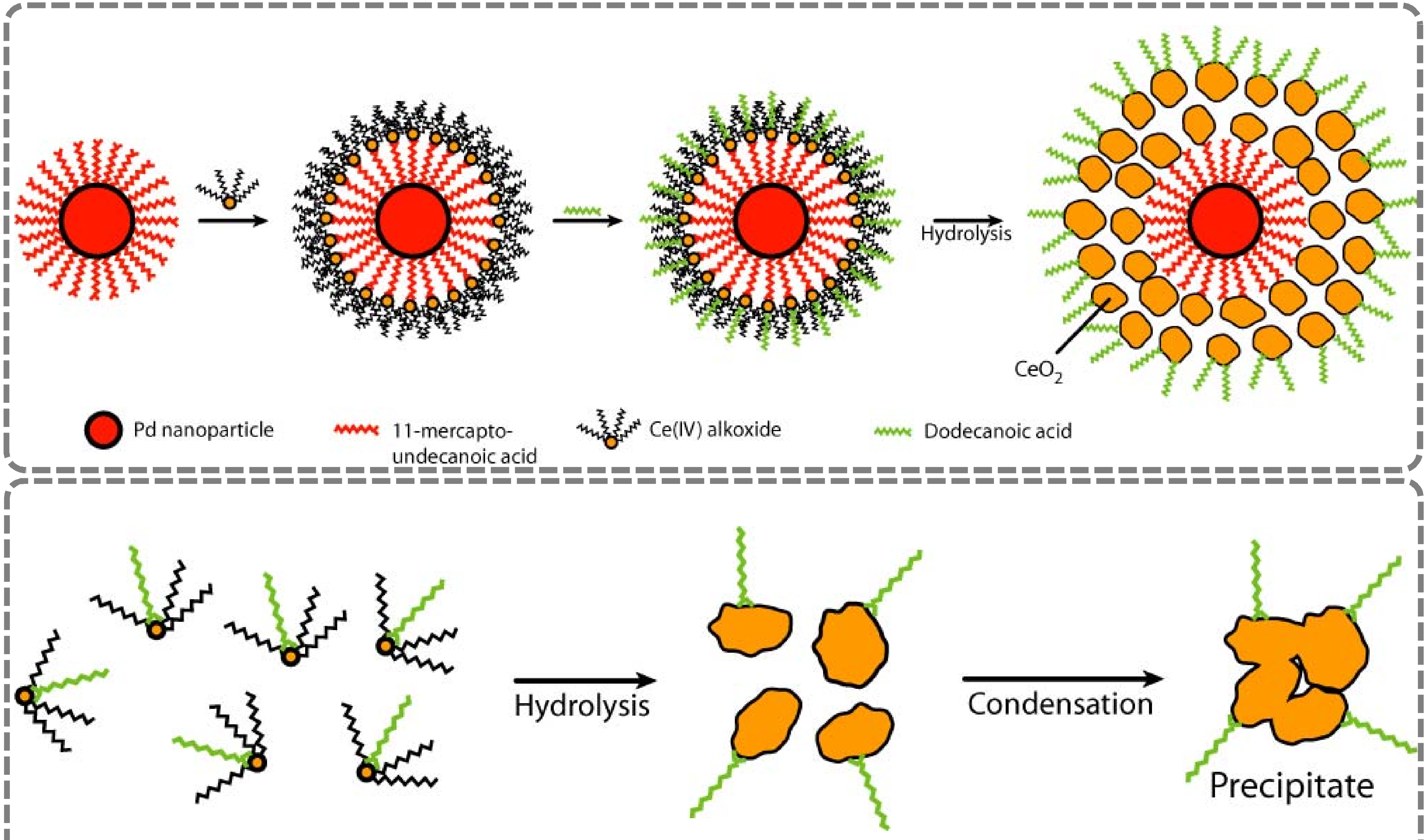
= dodecanoic acid-modified Ce(IV) tetrakis(decyloxide)



Hydrolysis conditions:
THF + 30 eq H_2O
(120 mol vs Ce) in 4 h

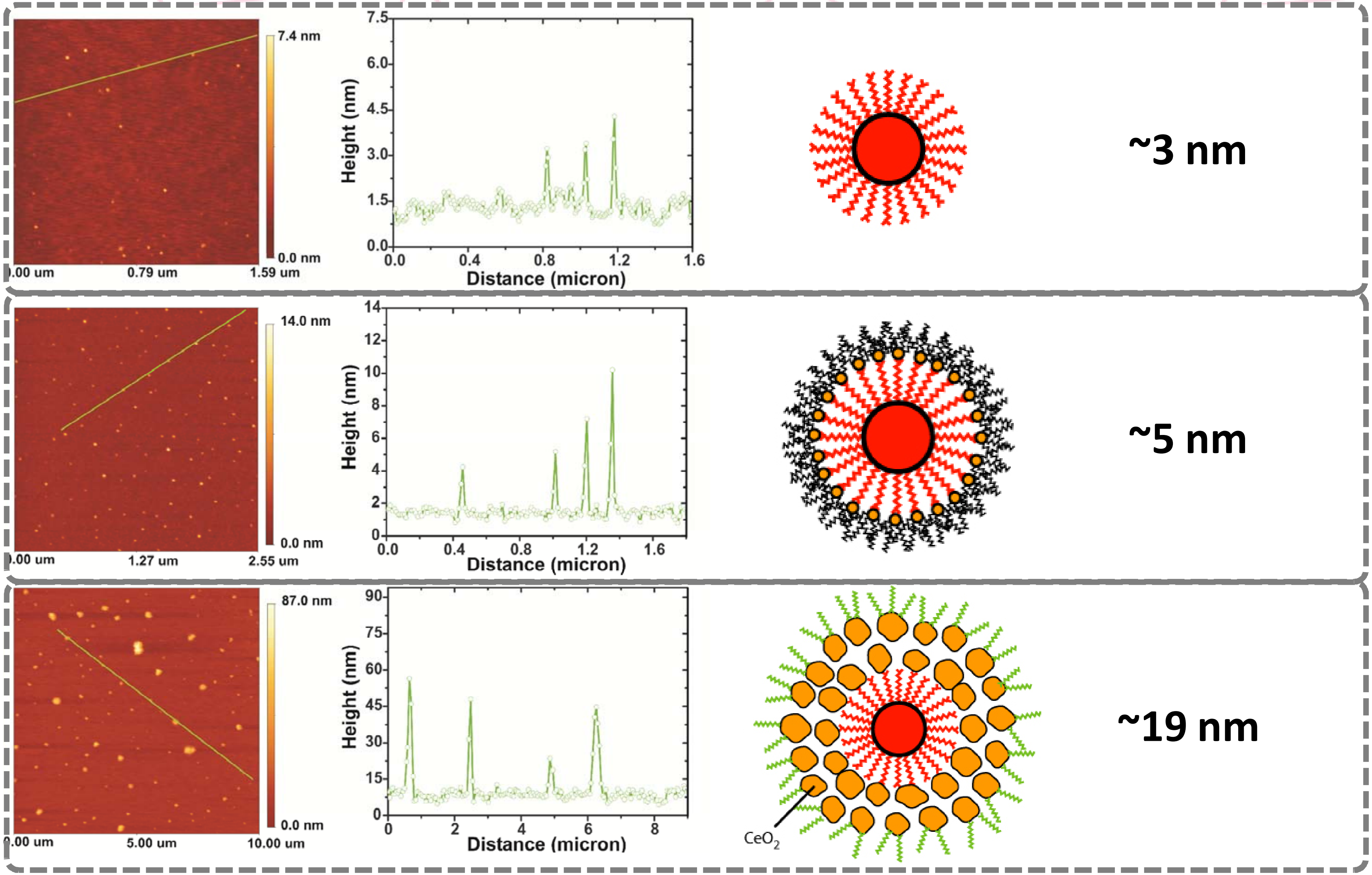
Dispersible in CH_2Cl_2, toluene, hexane

TEMPLATING EFFECT

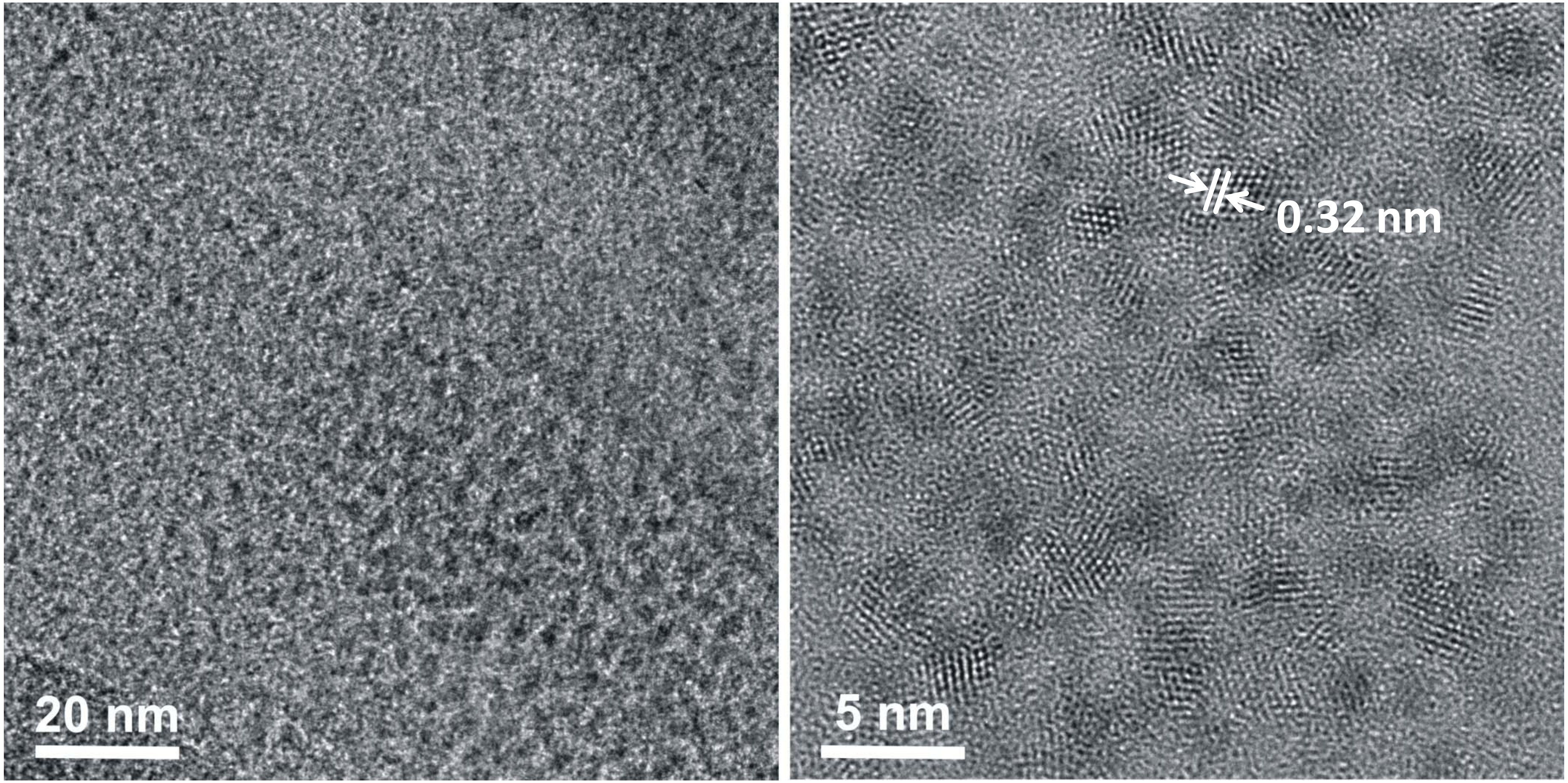


J. Am. Chem. Soc. **2010**, *132*, 1402

CHARACTERIZATION OF $Pd@CeO_2$ DISPERSIBLE ASSEMBLIES: ATOMIC FORCE MICROSCOPY

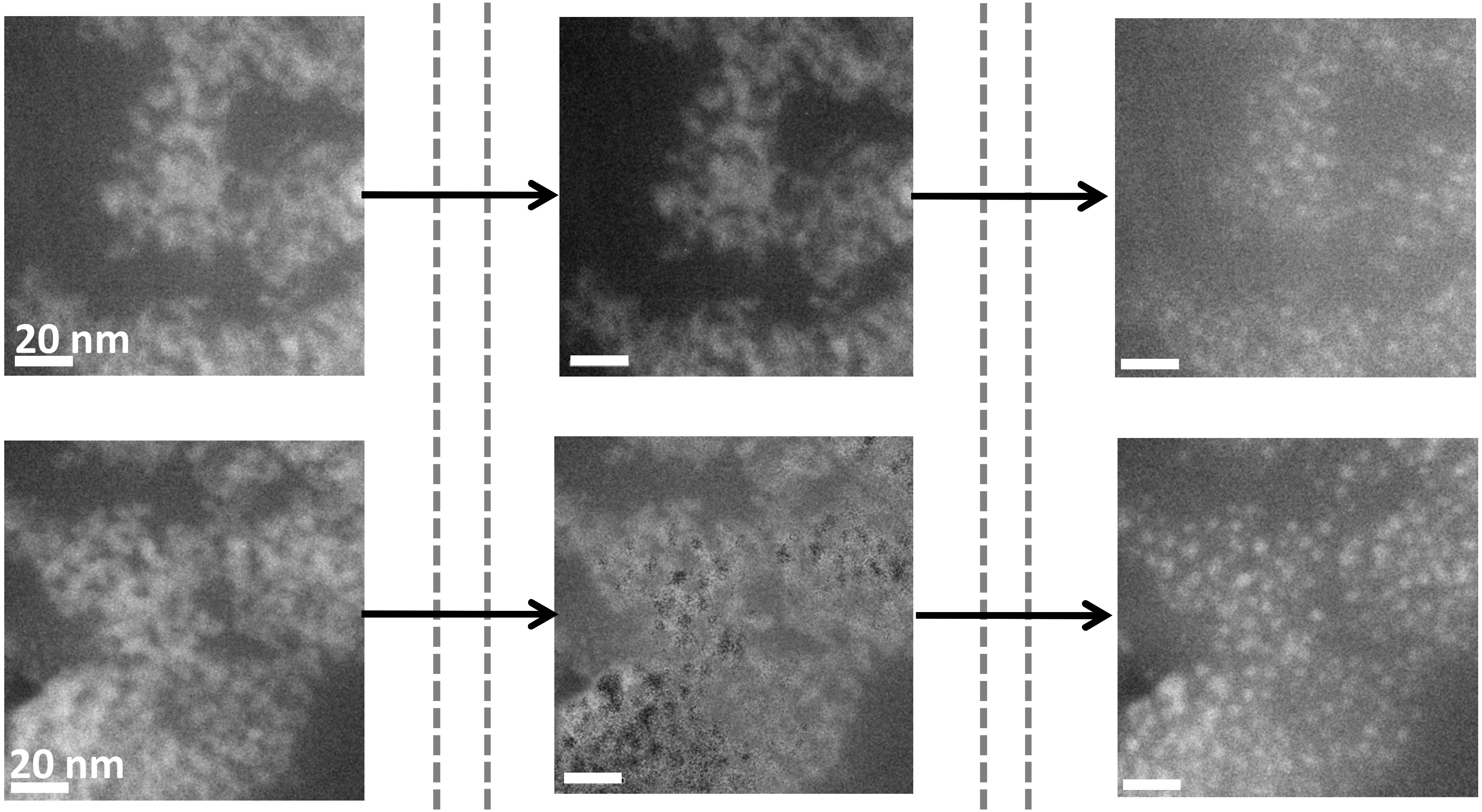


CHARACTERIZATION OF Pd(50%)@CeO_2 DISPERSIBLE ASSEMBLIES: TEM



Very small CeO_2 nanocrystals. And Pd?

CHARACTERIZATION OF Pd(50%)@CeO_2 DISPERSIBLE ASSEMBLIES: EELS MAPPING

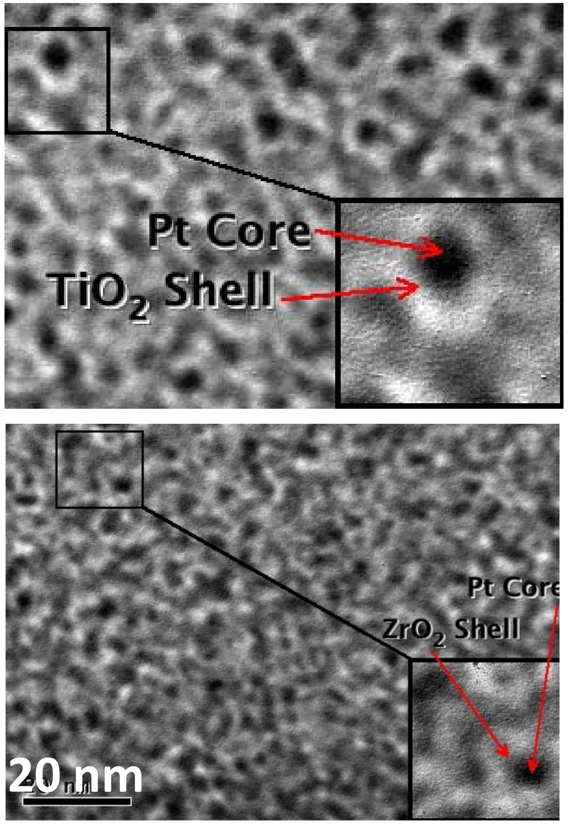


Ce post-edge:
S, Pd, Ce

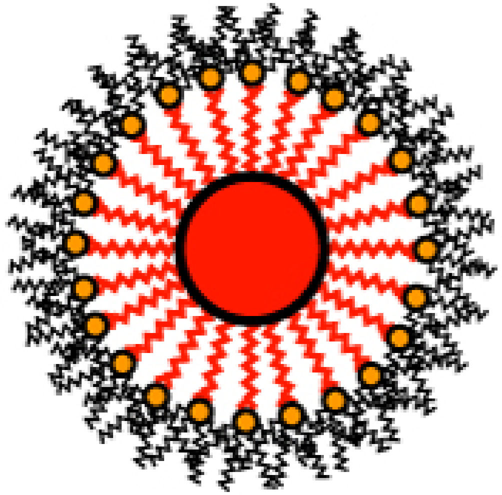
Ce map

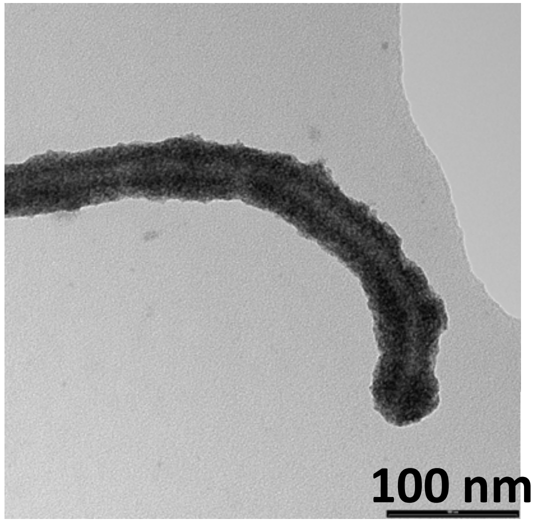
Ce pre-edge:
S, Pd

EXTENSION TO OTHER METAL@OXIDE COMBINATIONS



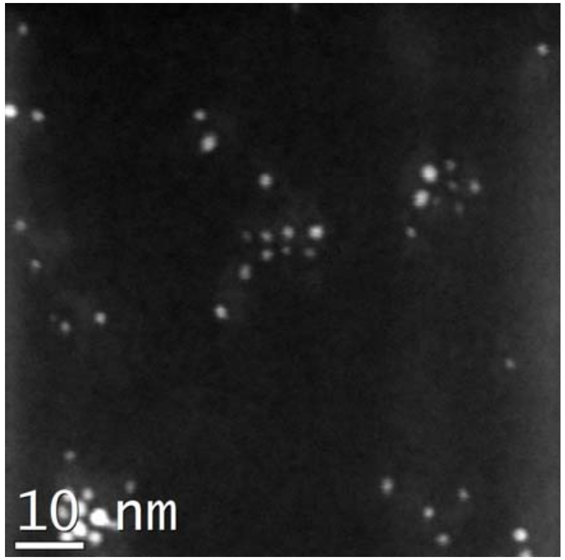
Shell oxide:
ZrO_2, TiO_2





Pd@CeO_2@CNTs

Core metal:
Pt, Pd-M
bimetallic
particles



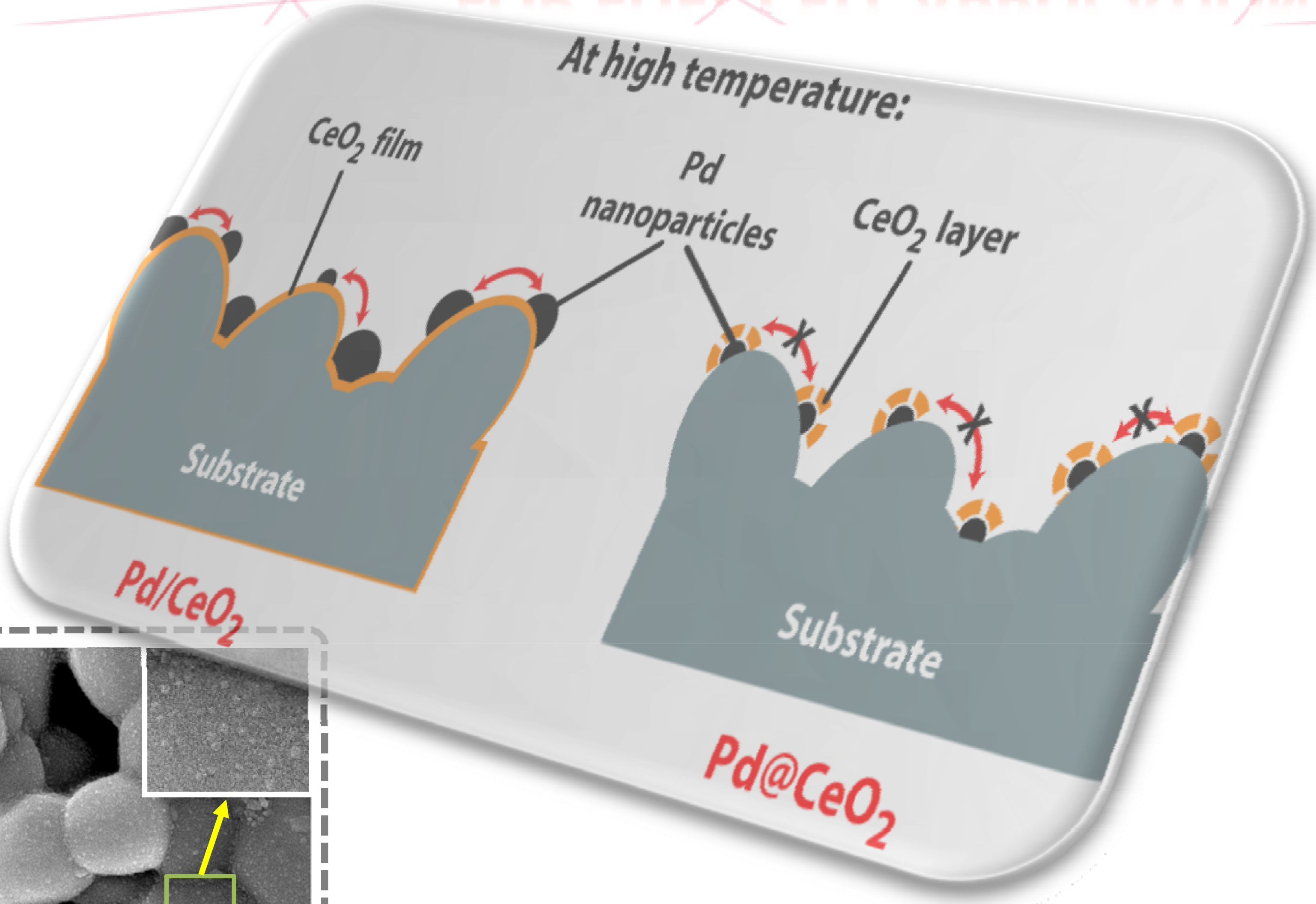
MUA-Pd/Au 1/1

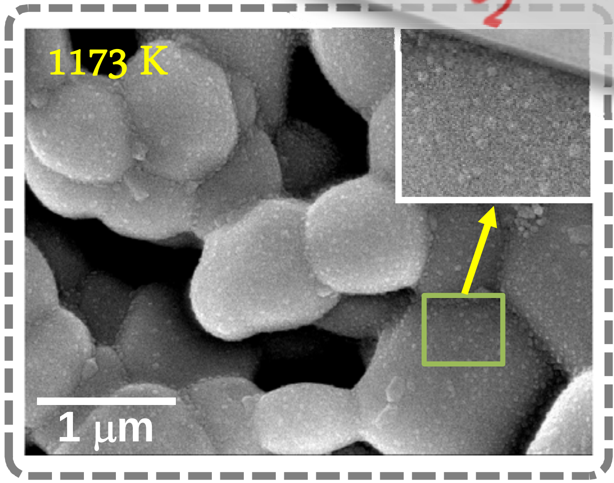
TAKE HOME MESSAGE #1

Simple preparation of dispersible core-shell structures with more "active" supports

???

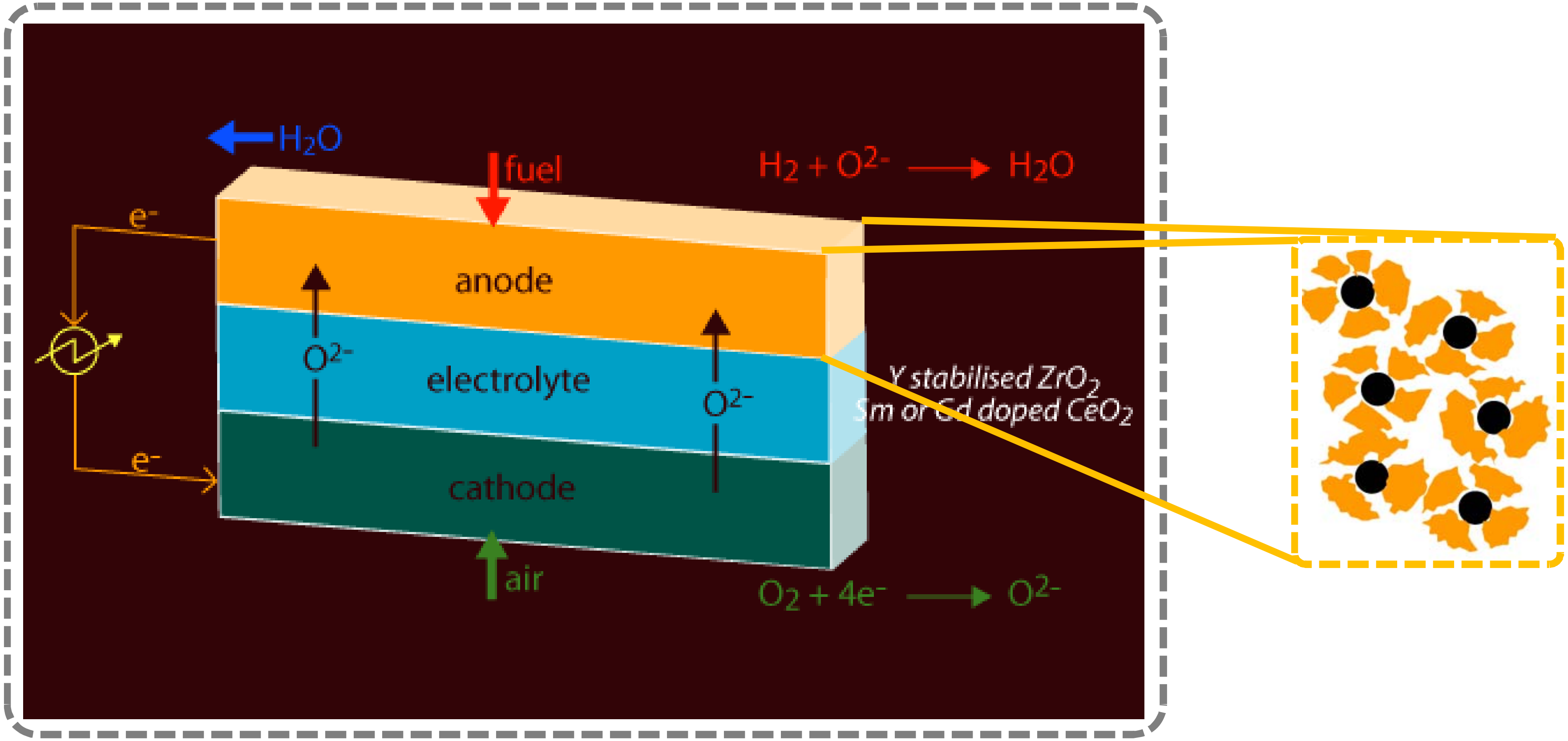
$Pd@CeO_2$ AS STABLE CATALYSTS FOR FUEL CELL APPLICATIONS





$Pd@CeO_2$/LSCM/YSZ

SOLID OXIDE FUEL CELLS: INTRODUCTION



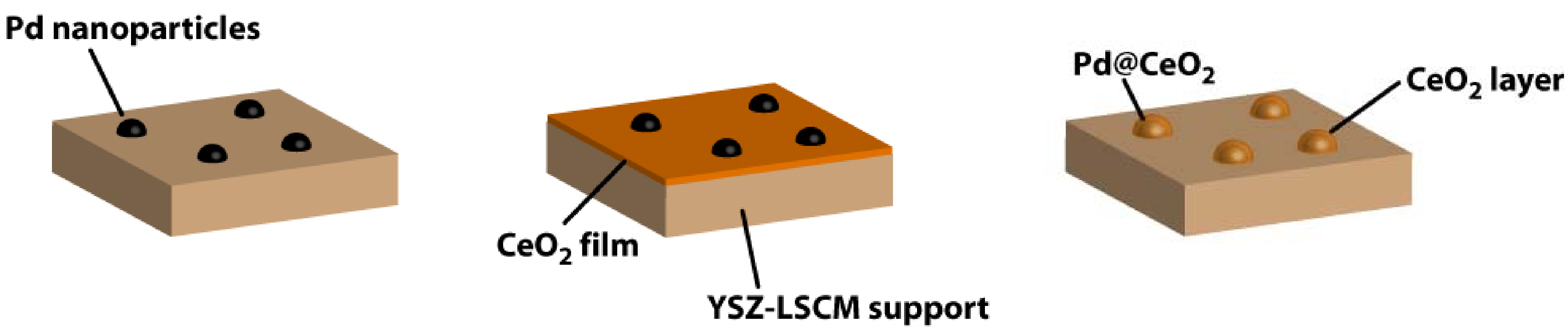
- all solid state
- high power densities
- possibility to use hydrocarbon fuels

Very high T (~700 °C)
→ Stable materials!

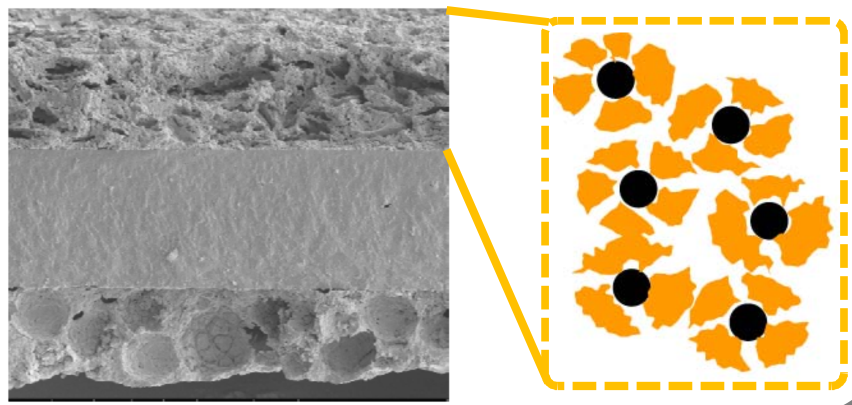
PREPARATION OF THE ANODE MATERIALS

Infiltration on anode materials

$Pd(NO_3)_2$	$Pd(NO_3)_2 + Ce(NO_3)_3$	$Pd@CeO_2$ nanostructures
Pd only	Pd/CeO_2	$Pd@CeO_2$

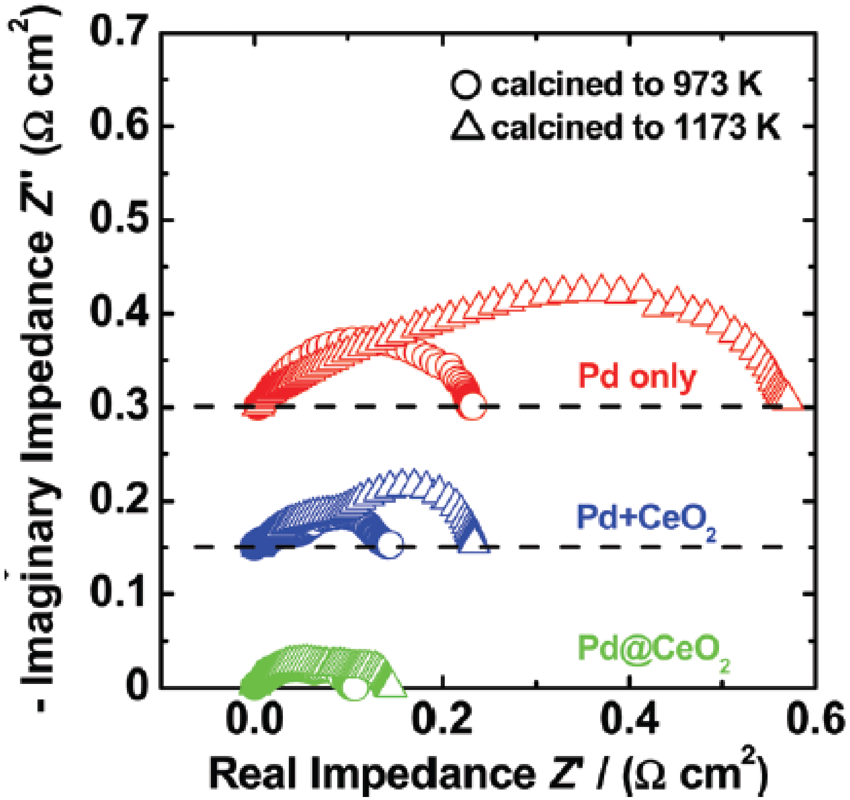


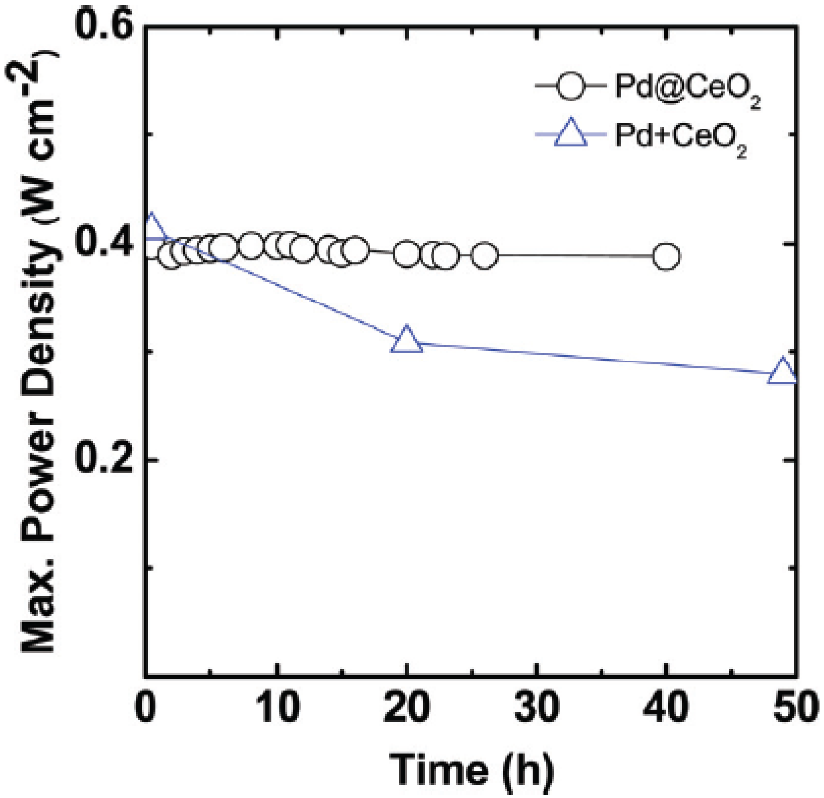
- 0.5 wt % Pd & 4.5 wt % CeO_2
- Calcination at 700 °C after infiltration
- Aging test: calcination at 900 °C



CATALYTIC ACTIVITY OF THE MATERIALS

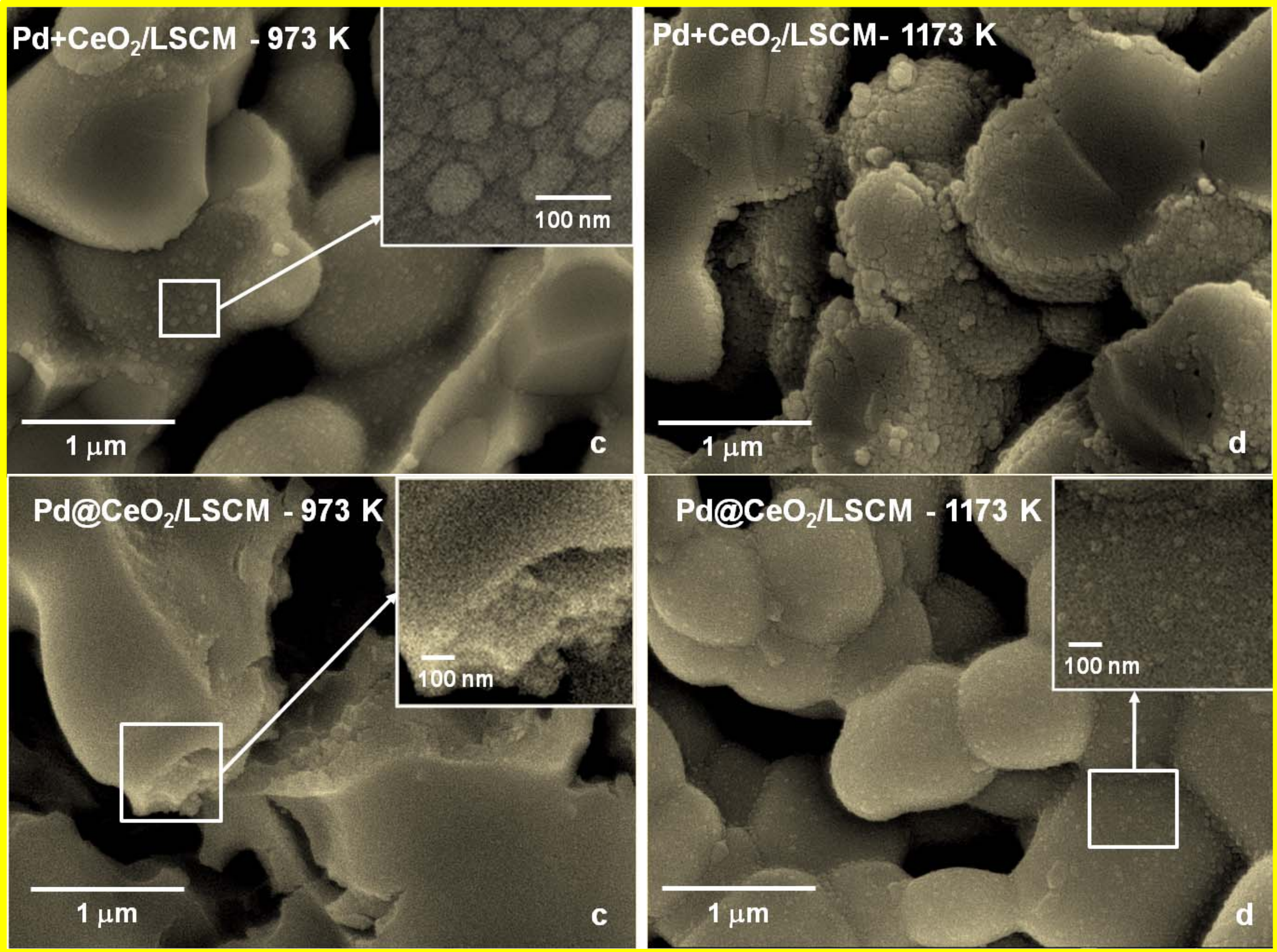
Symmetric or complete fuel cells,
in humified H_2 (3% H_2O) @ 700 °C



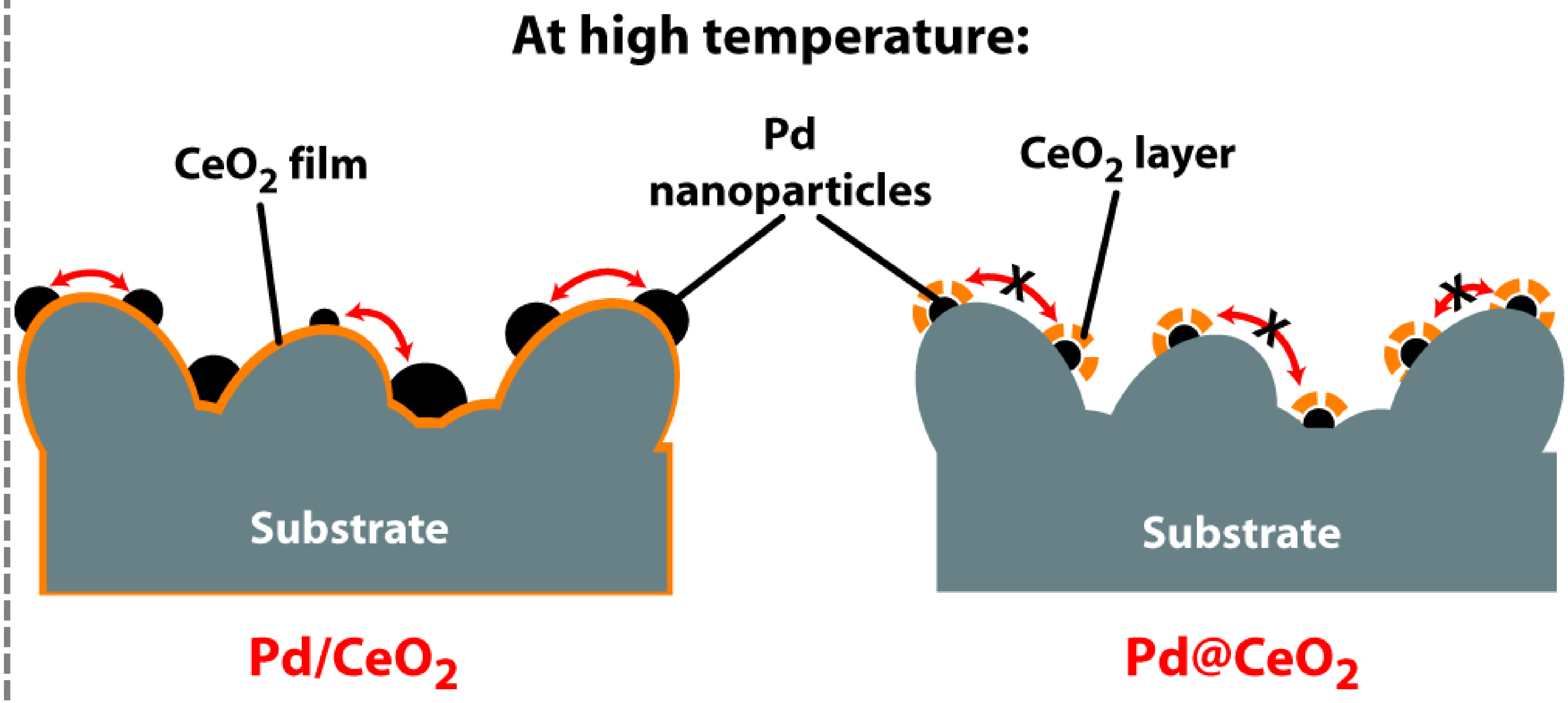


CHARACTERIZATION OF THE ANODES

FE-SEM



STABILITY OF Pd@CeO_2 CATALYSTS

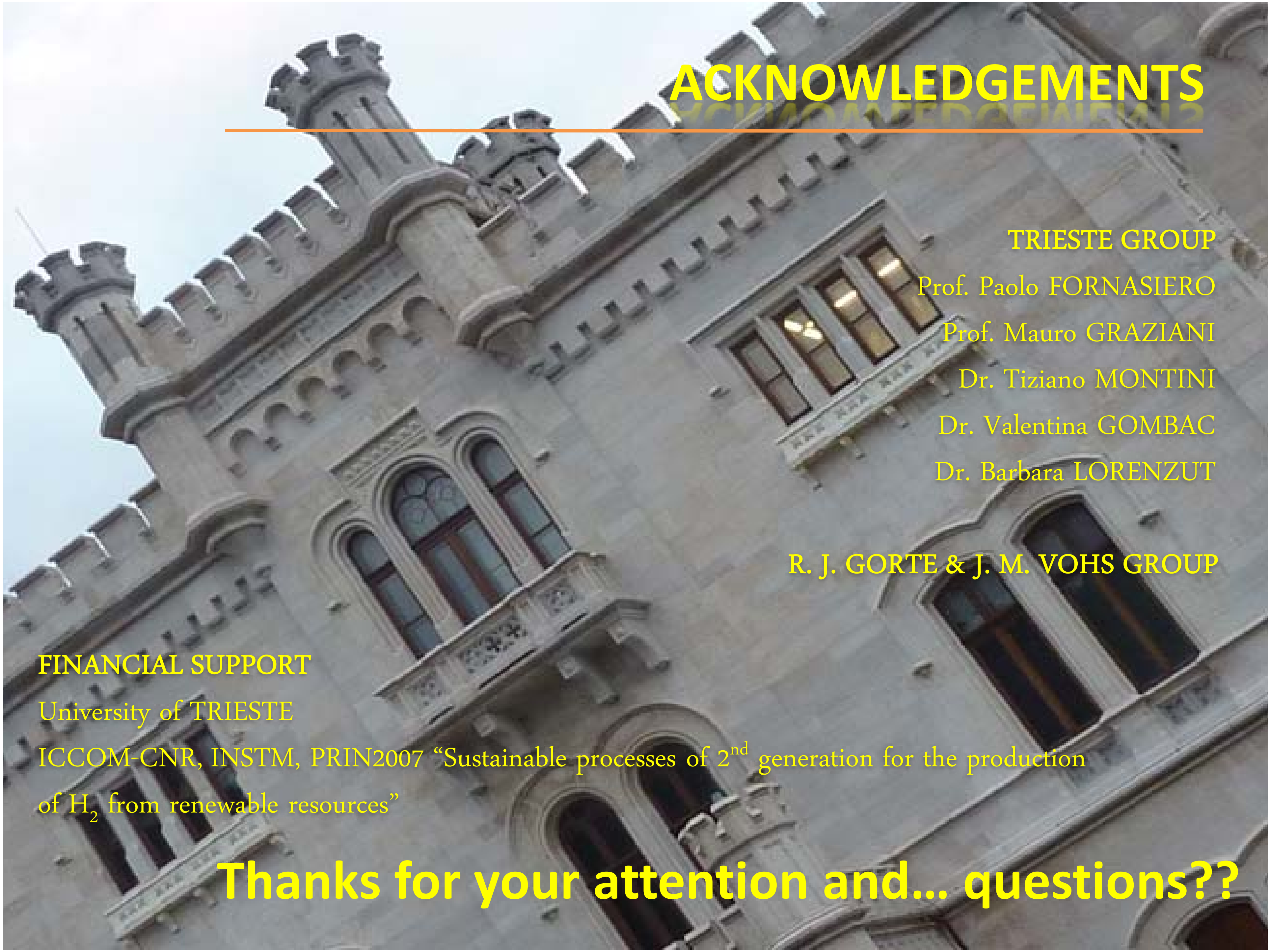


J. Electrochem. Soc. **2011**, *158*, B596

TAKE HOME MESSAGE #2

Simple preparation of dispersible core-shell structures with more “active” supports

The embedding approach can lead to highly active and thermally stable catalysts



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ICCOM-CNR, INSTM, PRIN2007 “Sustainable processes of 2nd generation for the production of H_2 from renewable resources”

Thanks for your attention and… questions??