X-ray Characterization of Mixed-Metal Oxides for the Photocatalytic Splitting of Water

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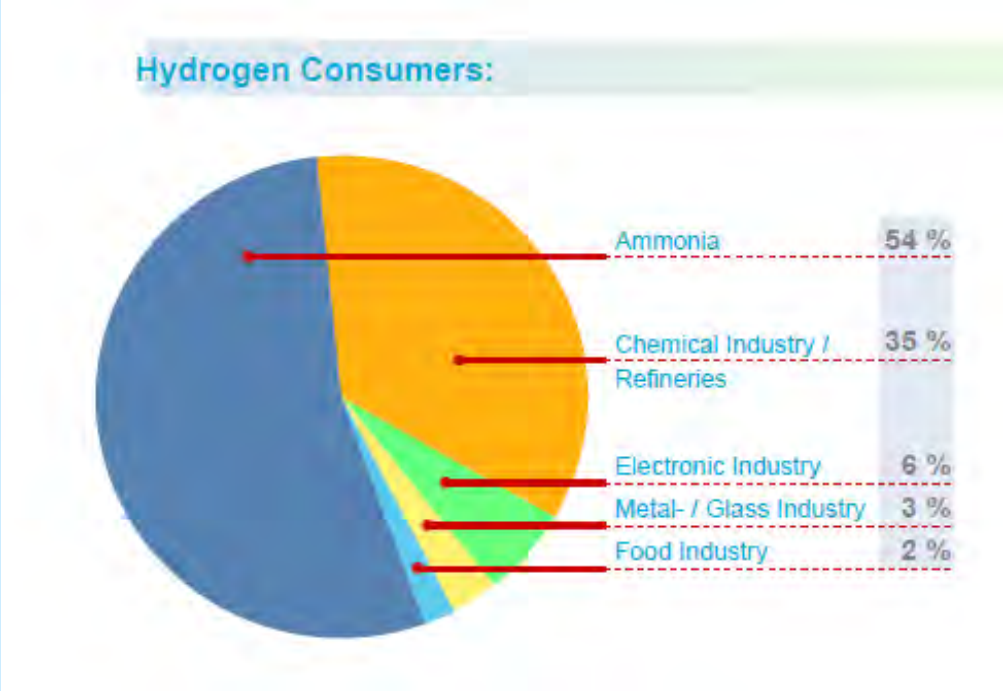
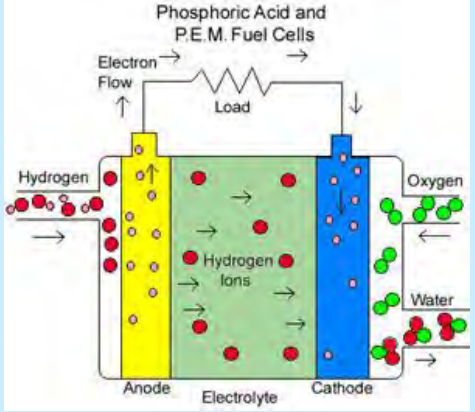
$ US-DOE

Outline

- Motivation/objective
- Photocatalytic splitting of water on $Pt/CeO_x/TiO_2$
- Morphological and structural properties of CeO_x/TiO_2
- Electronic properties of the ceria-titania interface
- *In situ* studies

Motivation: Hydrogen has many technological applications

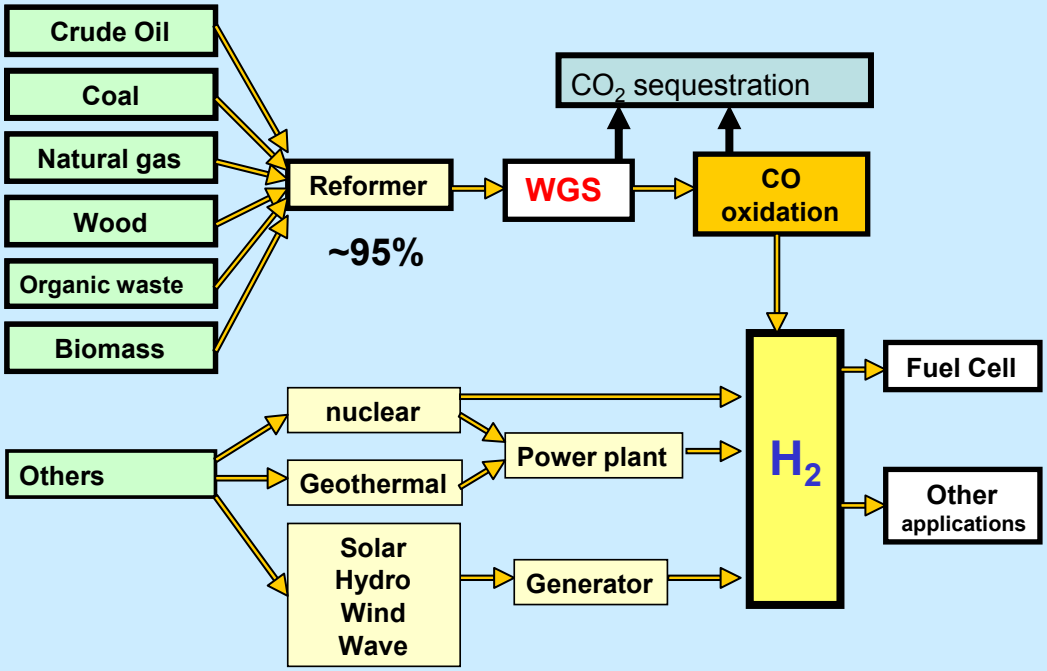




Novel applications:
Automotive fuel, fuel cells

Hydrogen plays a central role in the production of chemicals, foods and energy transformations

Motivation:



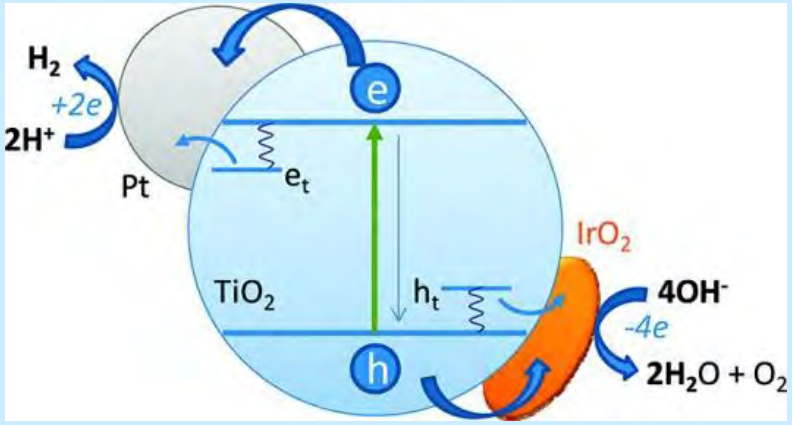
Most hydrogen is currently derived from the steam reforming of hydrocarbons:

$$C_nH_m + nH_2O \rightarrow nCO + (n\text{-}m/2)H_2$$

The reformed fuel contains 1-10% CO, which degrades the performance of the Pt electrode used in fuel cell systems.

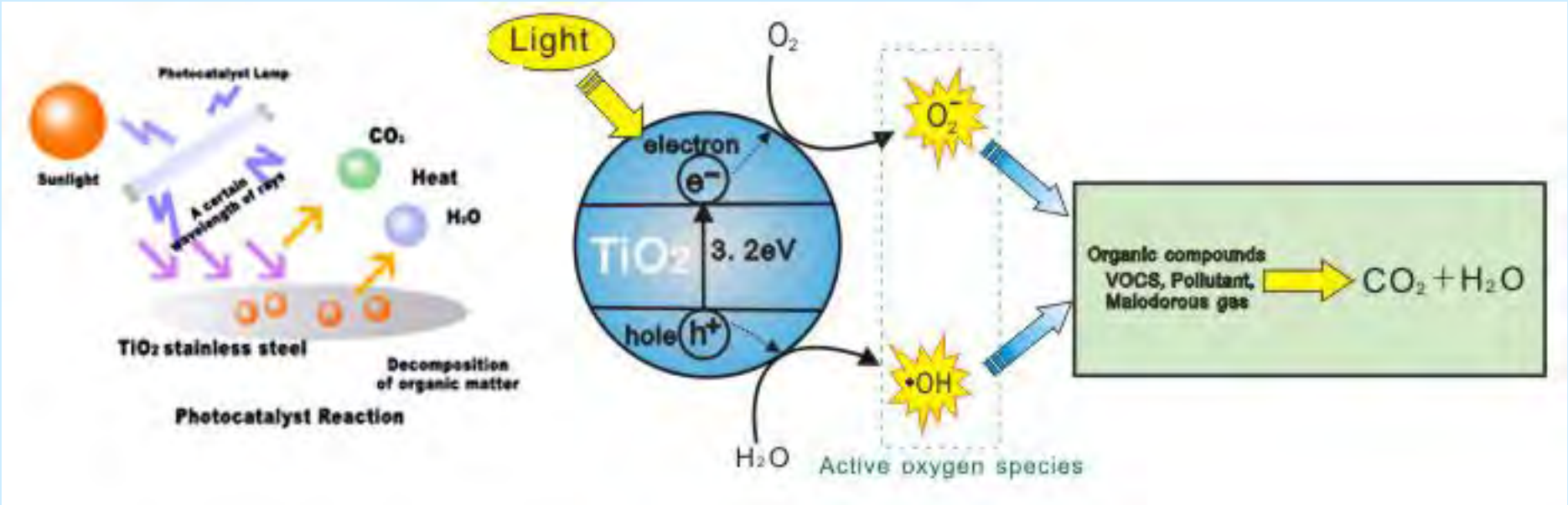
The photocatalytic splitting of water ($H_2O \rightarrow H_2 + 0.5O_2$) is an ideal approach for hydrogen production.

Photocatalytic splitting of water:



www3.nd.edu

Photocatalytic decomposition of pollutants:



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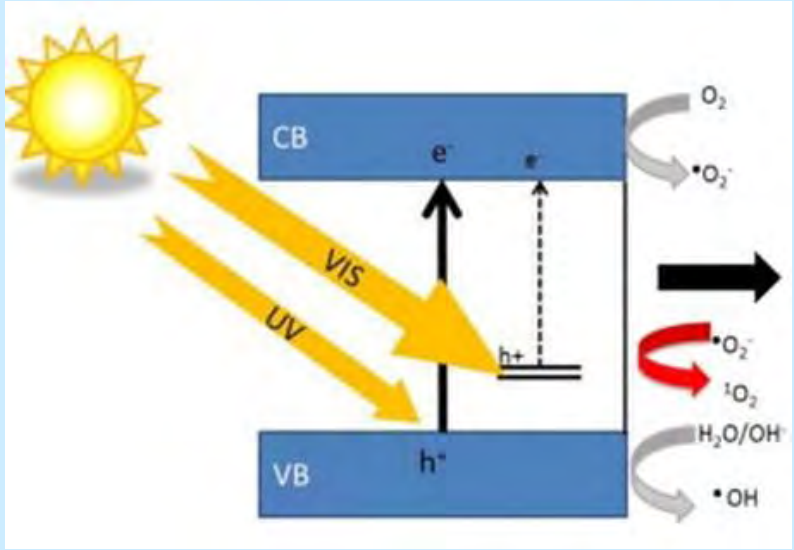
Photocatalytic splitting of water:



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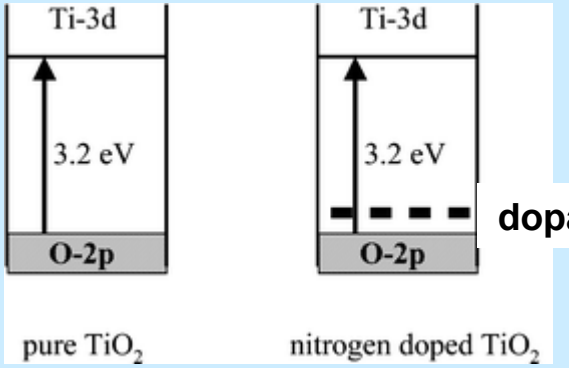
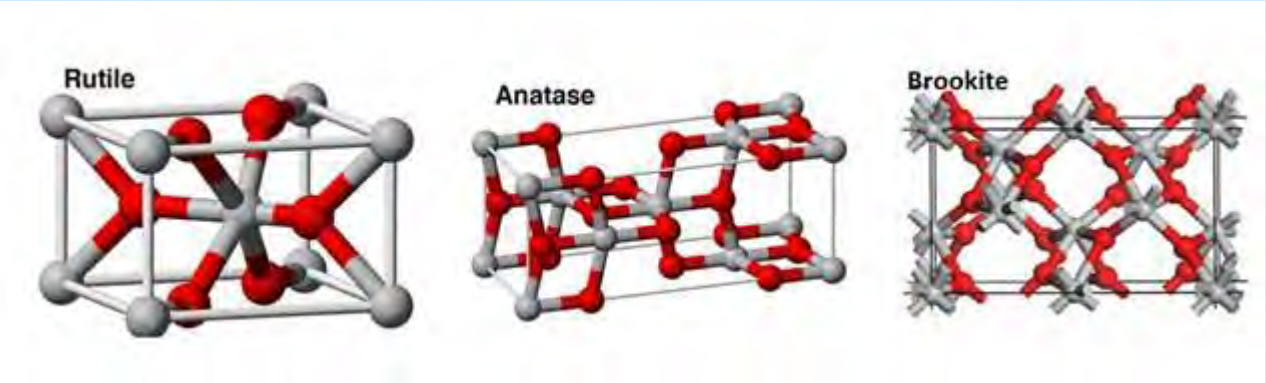
Titania with a band-gap of 3.2 eV absorbs mainly light in the UV region



dopant levels

Reduction of titania band-gap:

Substitutional doping:



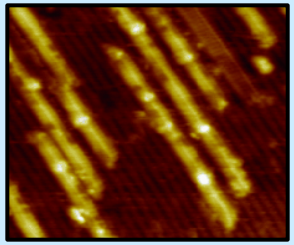
O → N, S, C

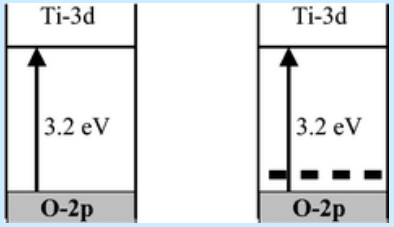
Ti → Ru, Mo, Fe …

Approach of BNL Catalysis Group: Oxide nanoparticles on titania

$CeO_x/TiO_2(110)$
JPCC **(2013)**

$RuO_2/TiO_2(110)$
Angew. Chem. Int. Ed. **(2011)**



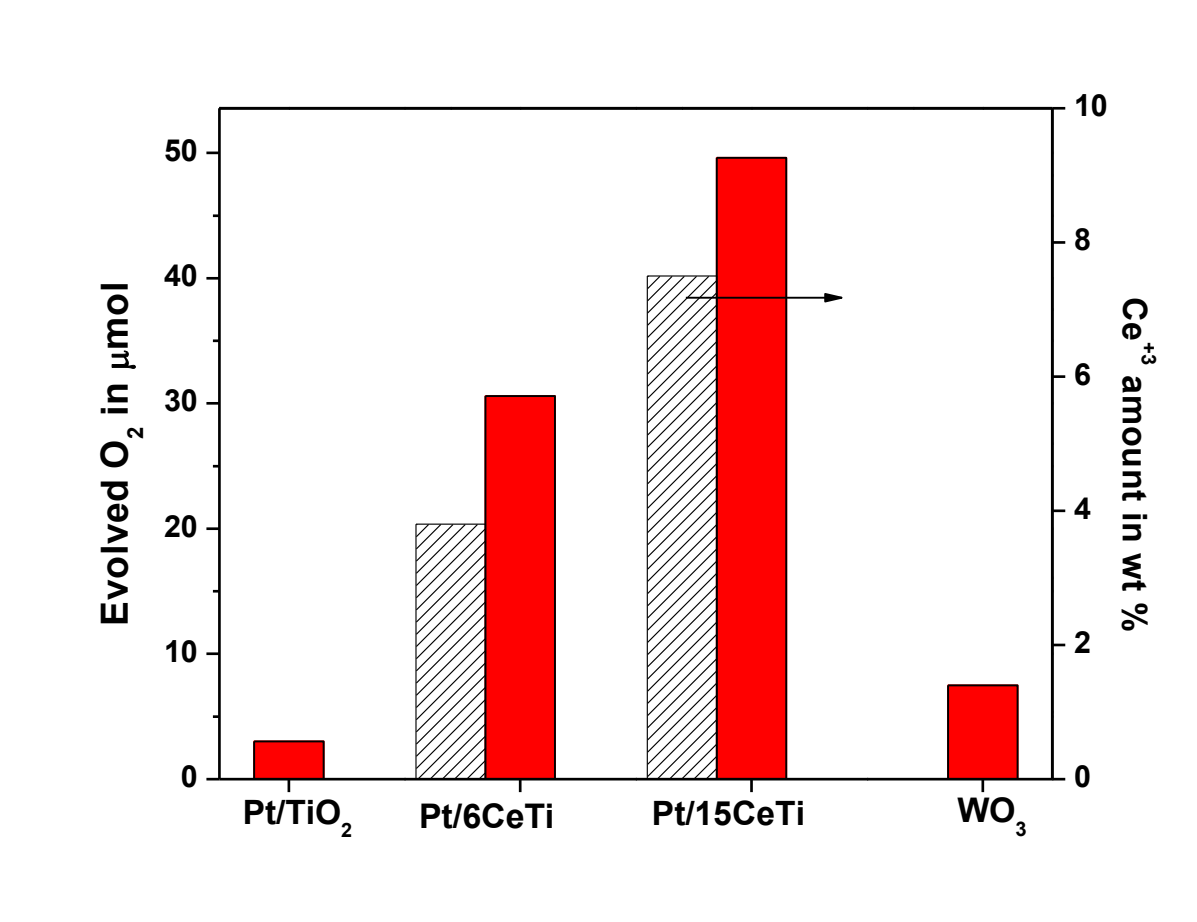


dopant levels

Pure TiO_2

Mixed-metal oxide

Photocatalytic splitting of water on $Pt/CeO_x/TiO_2$



$Pt/CeO_x/TiO_2$ better photocatalyst than WO_3 standard.

The left axis and red bars show the amount of oxygen evolved on Pt/TiO_2, $Pt/CeO_2/TiO_2$ and WO_3 catalysts from water photo-oxidation upon visible light (λ >400nm) illumination for 4 hours. The right axis displays the amount of Ce^{+3} present in the $Pt/CeO_2/TiO_2$ catalysts calculated from the corresponding Ce M-edge NEXAFS spectra obtained by PEY measurements.

Kundu et al, J. Phys. Chem. C, **2012**, *116*, 14062−14070

Why is CeO_x/TiO2 a better photocatalyst than TiO_2?

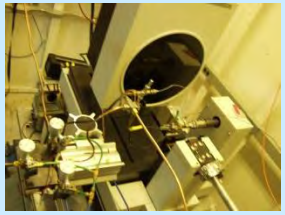
Fundamental studies on the nature of the oxide-oxide interface:

- **The properties of $CeO_x/TiO_2(110)$ surfaces**
- **The properties of CeO_x/TiO_2 powders**

National Synchrotron Light Source

Photoemission
(electronic)

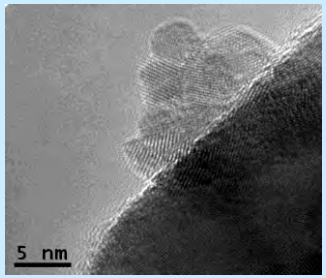
XAFS
(electronic, structure)



XRD, PDF
(structure)

Center for Functional Nanomaterials

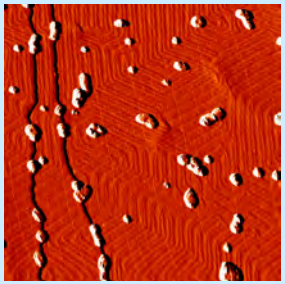
CeO_x/CuO



powder catalysts

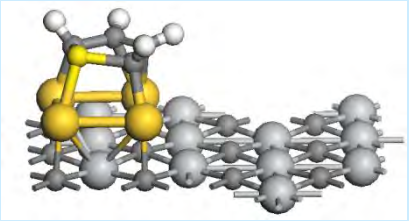
Environmental TEM

CeO_x/Au(111)



model single crystals

HR-STM, LEEM/PEEM, NAP-XPS

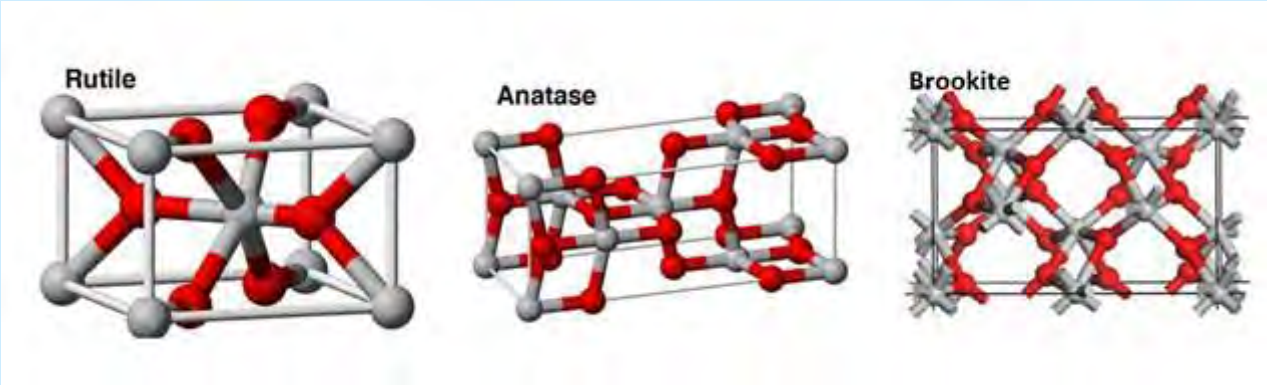


theoretical modeling

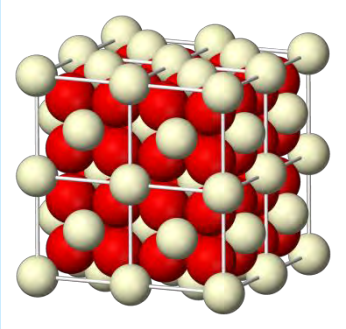
Computer facilities

Crystal Structures:

Titania:



Ceria



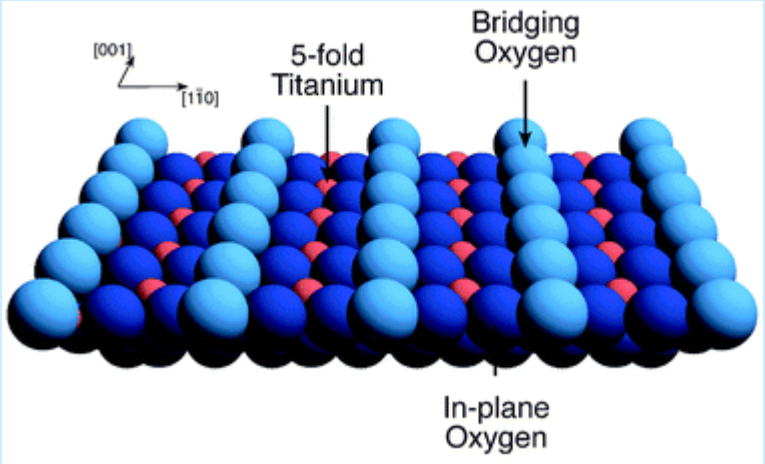
fluorite

Since the two oxides have different crystal structures, novel structures can occur at the oxide-oxide interface

Fundamental studies on the nature of the oxide-oxide interface:

- **The properties of $CeO_x/TiO_2(110)$ surfaces**

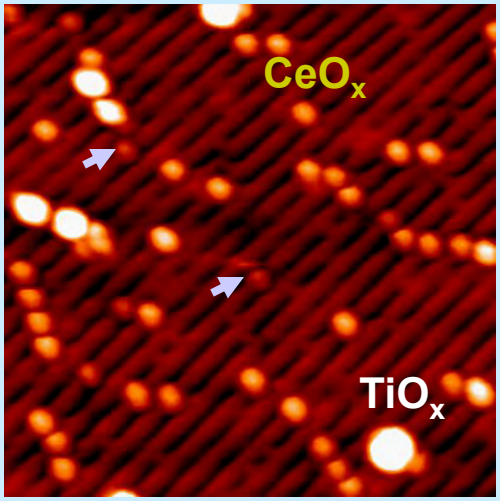
Ce + O_2

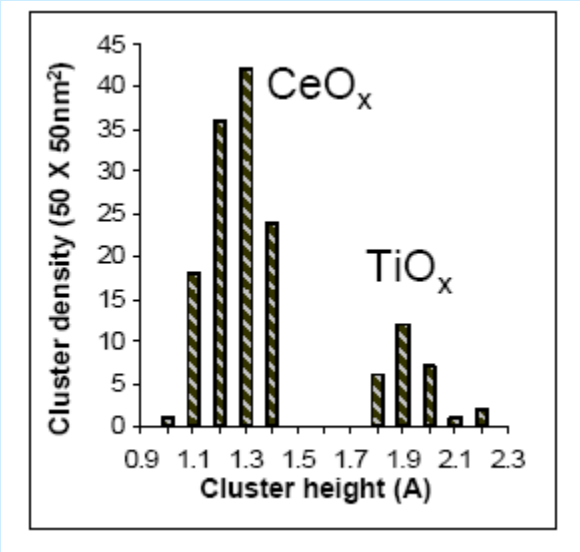


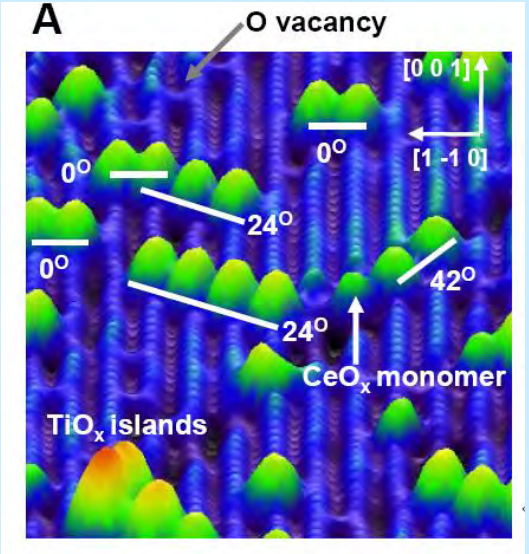
$TiO_2(110)$

CeO_x on $TiO_2(110)$

15 nm x 15 nm

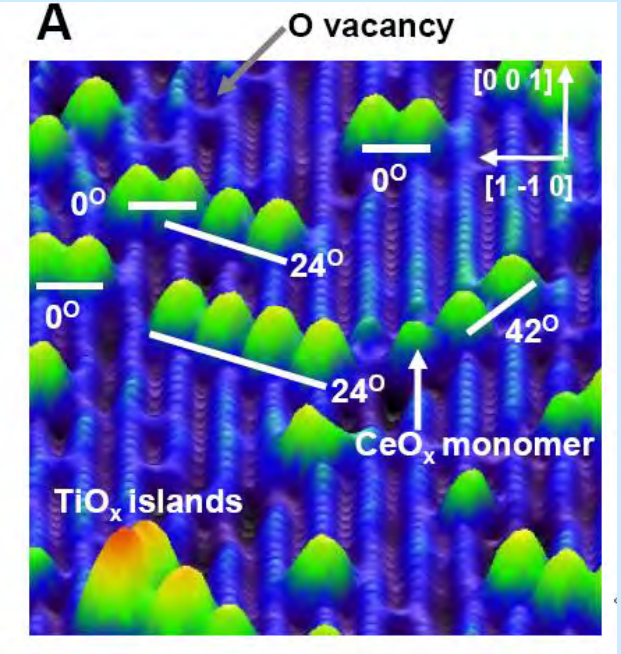


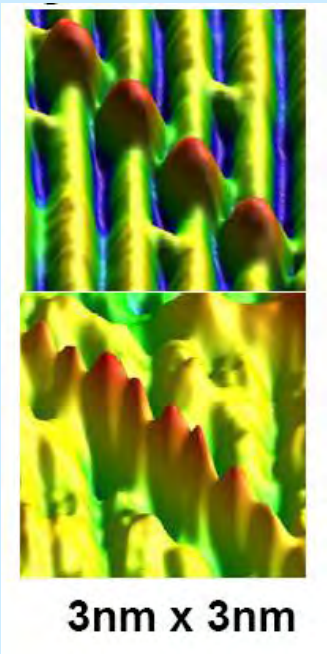




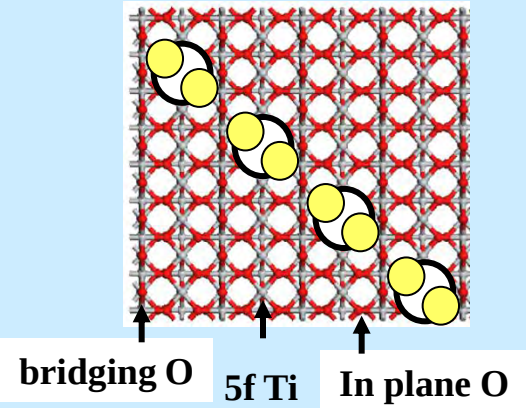
vapor deposition of Ce in P_{O2}=1.5x10^{-7}mbar at 600K. Then, the sample was heated at 900K for 5 min (P_{O2}:1.5x10^{-4}mbar).

Rodriguez et al, PNAS. 13 (2009) 4975

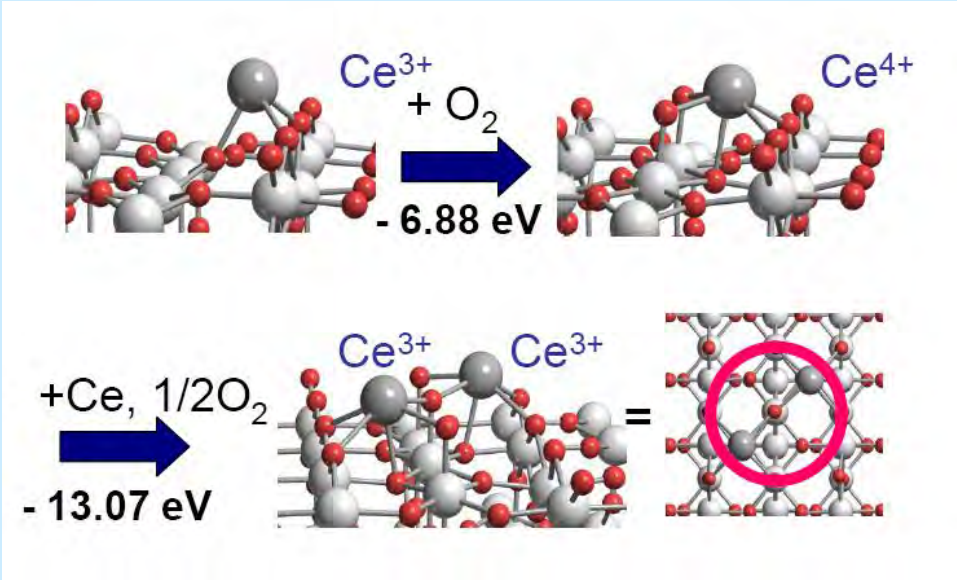




Ceria dimers ar basic units



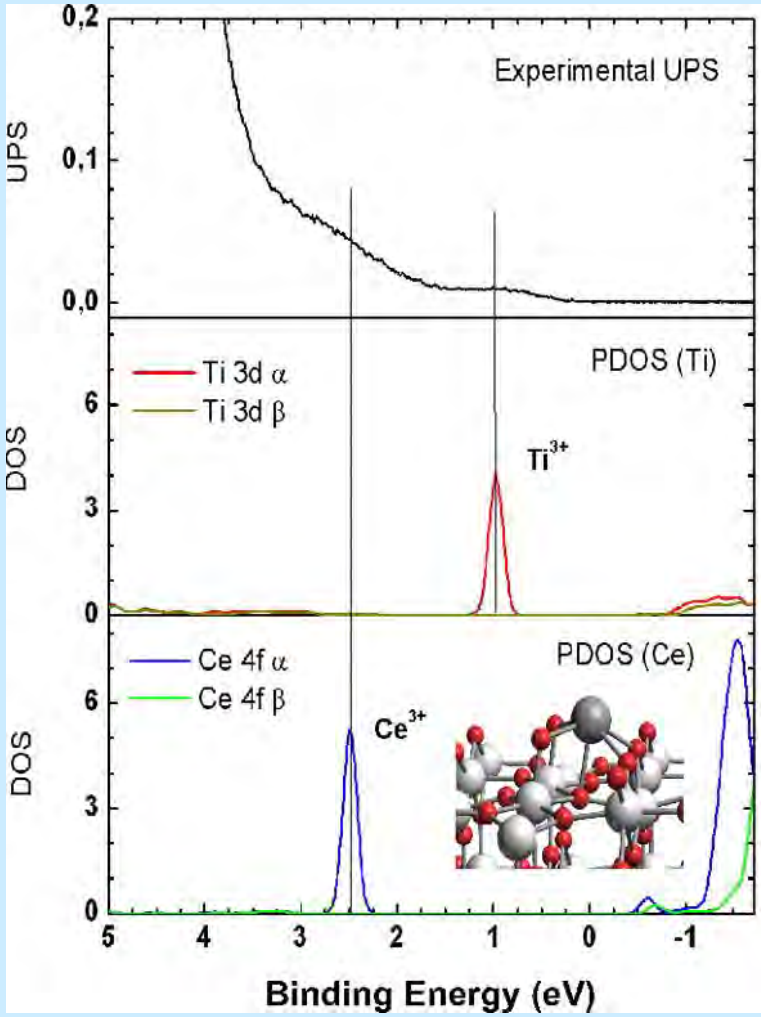
DFT results:

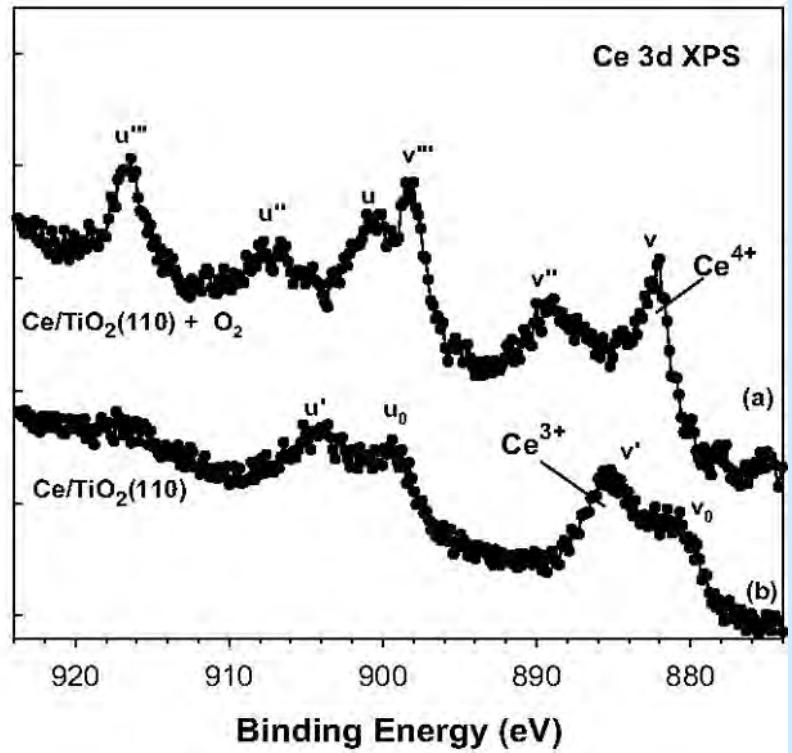


Titania substrate imposes non-typical coordination modes on the ceria NPs

Rodriguez et al, PNAS. 13 (2009) 4975

Valence and core photoemission

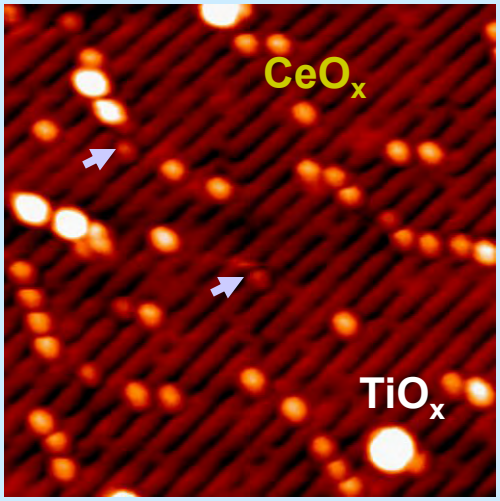


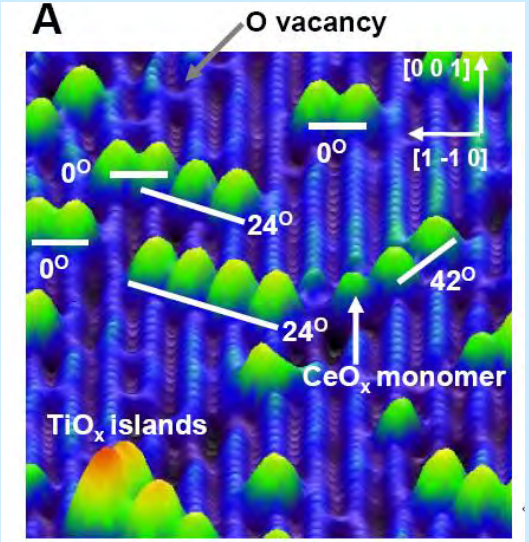


Rodriguez et al, PNAS. 13 (2009) 4975

CeO_x on $TiO_2(110)$

15 nm x 15 nm





Rodriguez et al, PNAS. 13 (2009) 4975

→ **Powder catalyst?**

Fundamental studies on the nature of the oxide-oxide interface:

- **The properties of CeO_x/TiO_2 powders**

Sample preparation

TiO_2 nano particles thermal treatment	
dry air	500°C

↓

Ce modified TiO2	
Wet impregnation	Aqueous solution of ceria nitrate

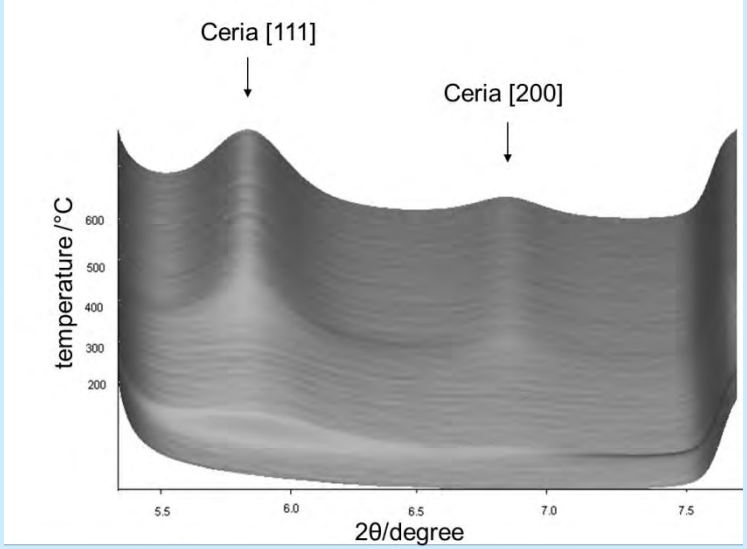
↓

Ceria modified catatyst	
Calcine at 600°C	O_2

The growth of the ceria nanoparticles on titania was studied *in-situ* using TEM (CFN) and XRD (NSLS I)

Growth study

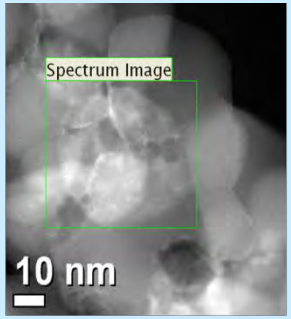
X7B
NSLS I

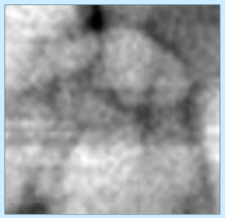


Time resolved XRD

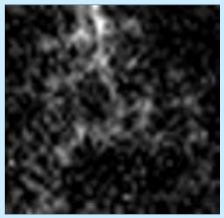
- Ce nitrate precursor dispersed well on the surface of TiO_2 NPs
- Small ceria nano crystals formed when calcined to around 200°C in O_2
- Crystallized ceria shows a growth of size from about 3nm to 6nm with continuous heating to 400°C

TEM
at CFN

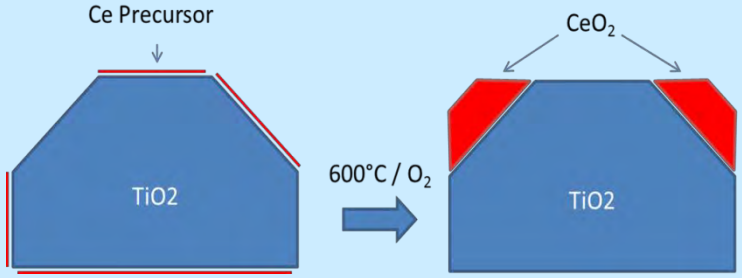


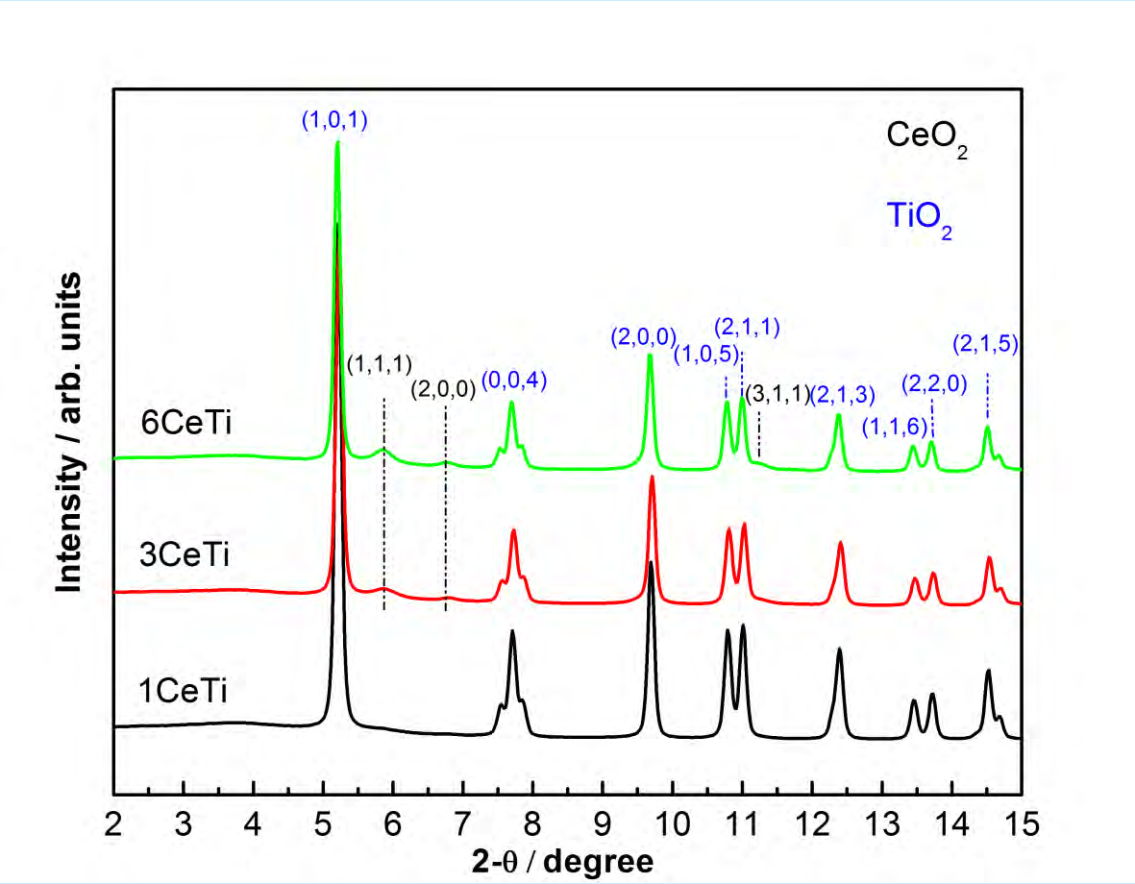


Ti map



Ce map





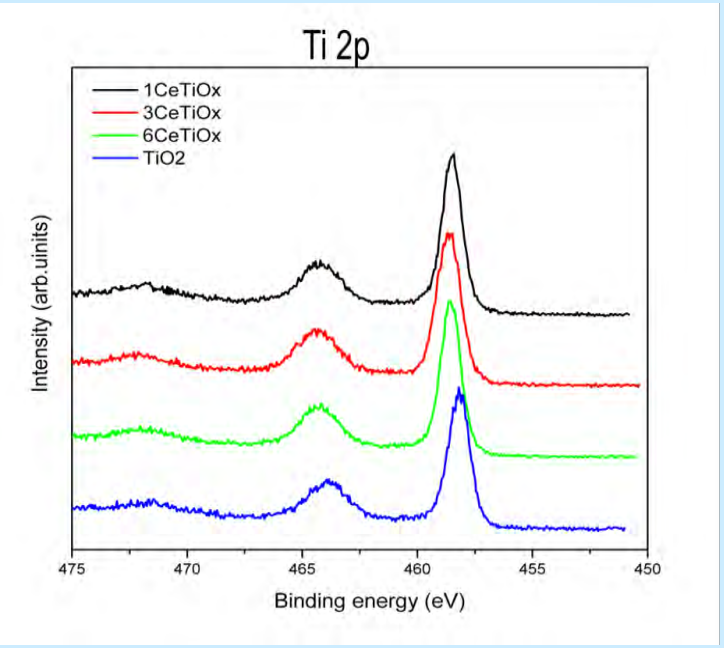
XRD characterization

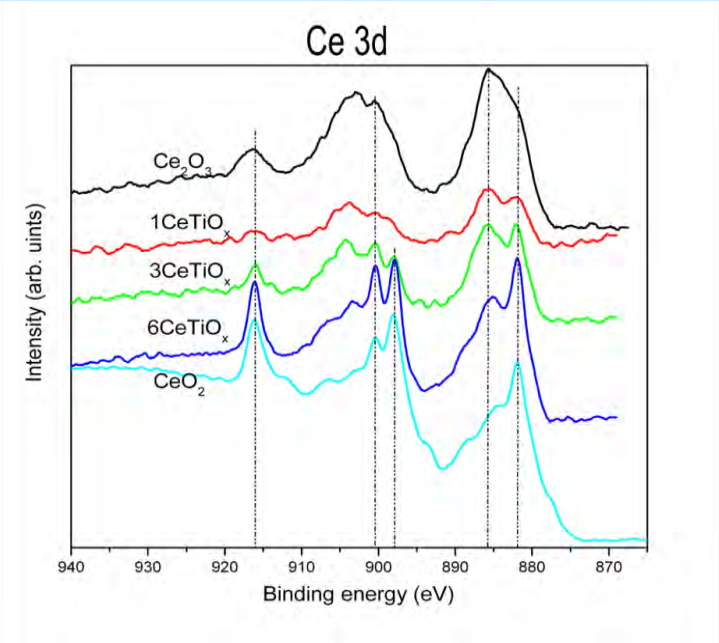
X7B beamline

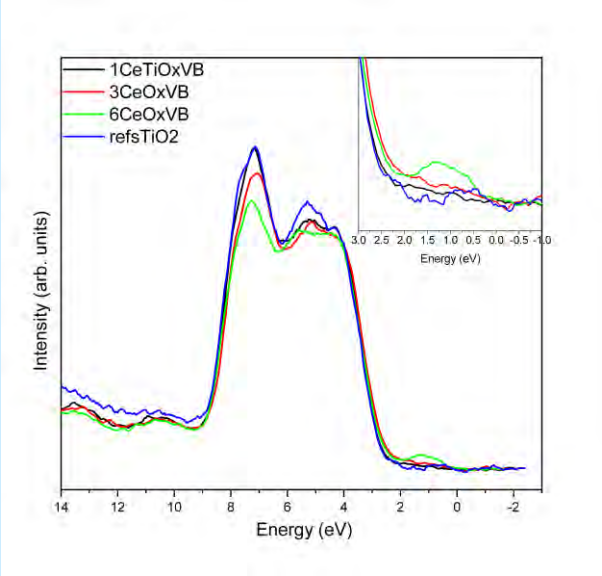
Samples	$1CeO_xTiO_2$	$3CeO_xTiO_2$	$6CeO_xTiO_2$
Ceria lattice (A)	5.436(6)	5.419(2)	5.413(1)
Ceria concentration	1.0(1)%	4.0(1)%	5.5(1)%
Ceria size	undetectable	4.8(5)nm	6.0(5) nm

5.421 A (bulk CeO_2)

Electronic properties: XPS



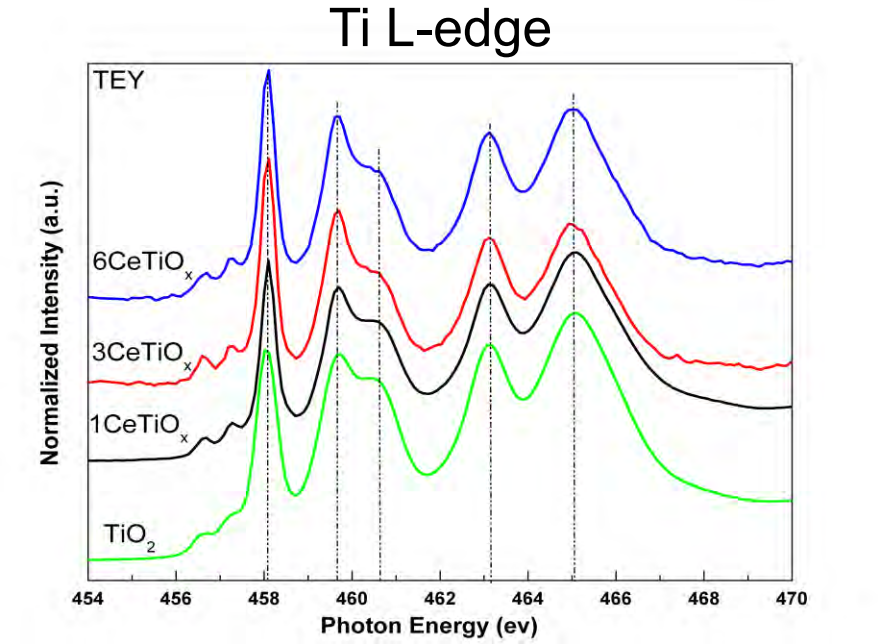


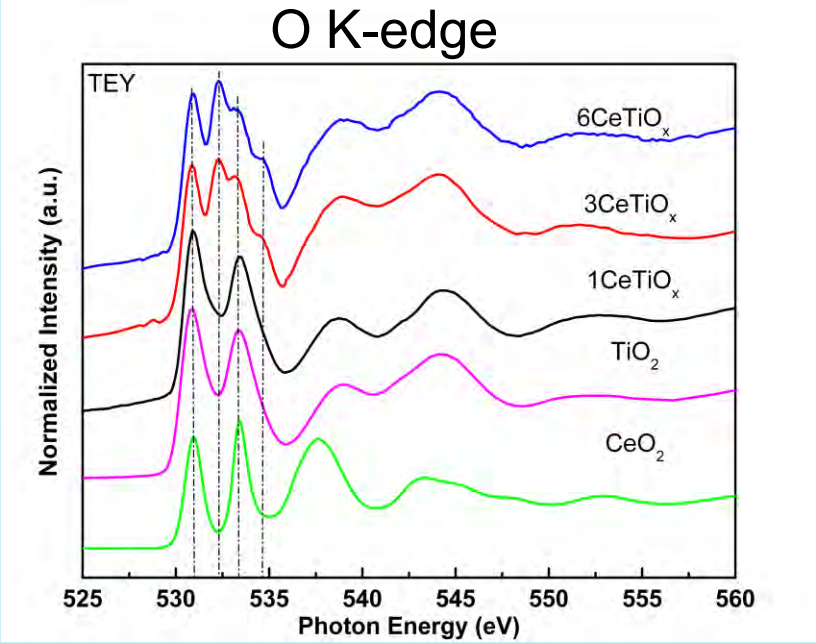


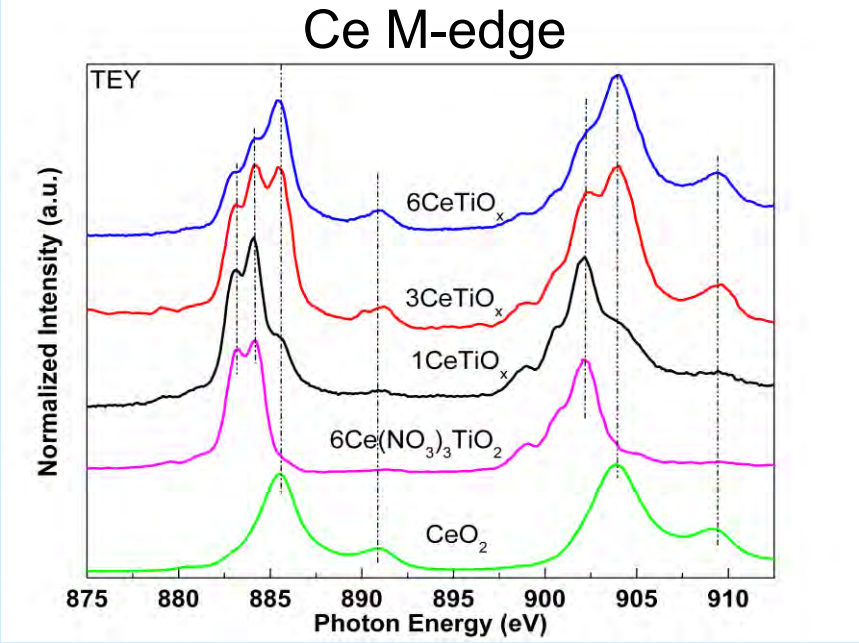
- Titanium in all the three samples is proved to be pure Ti^{4+}
- Cerium in sample with light loading ($1CeO_xTiO_2$) is mainly Ce^{3+} ions with minor Ce^{4+}
- $3CeO_xTiO_2$ sample has both Ce^{3+} and Ce^{4+} species
- New valence state shows up which is due to the influence of ceria doping

Electronic properties: NEXAFS

- TiO2 are present in anatase phase
- Ceria in sample with relatively higher loading (6wt%) is dominated by Ce^{4+} with minor Ce^{3+} features
- electronic property properties of sample probed by O K edge shows obvious perturbation by CeO_x

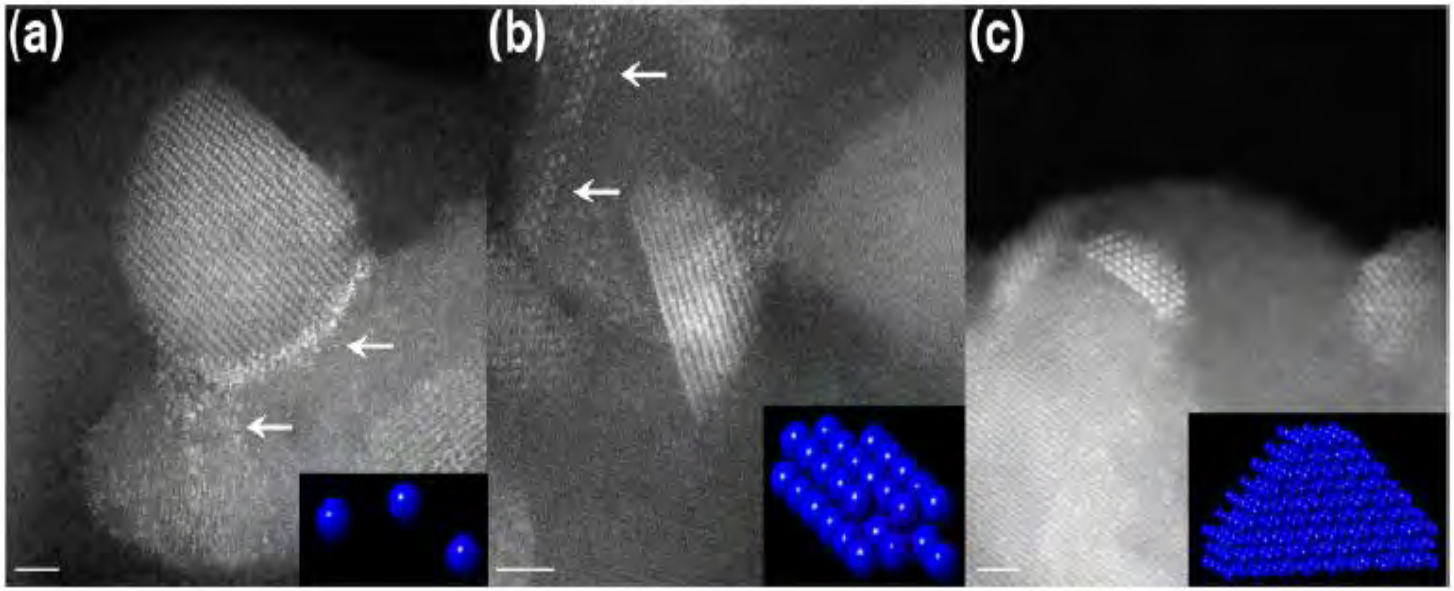






CeOx nanostructures on titania (anatase) powder

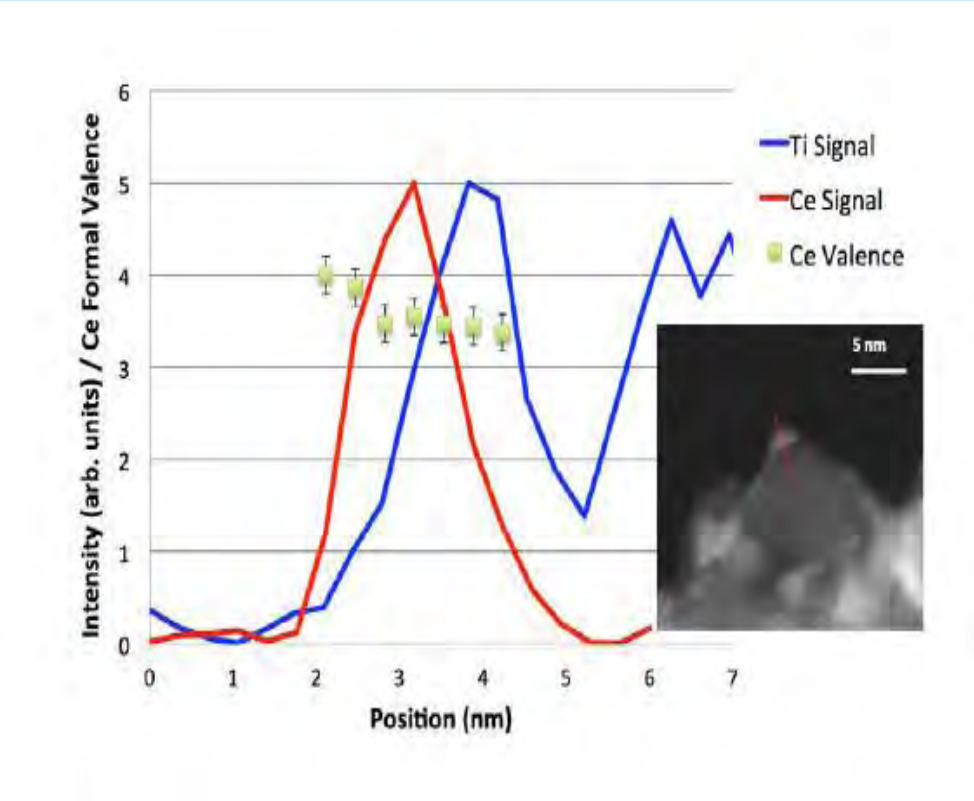
TEM
at CFN



HAADF STEM images showing the different morphologies of ceria that can be found in a CeOx/TiO2 sample: clusters (a), constrained structures (chains) (b), and nanoparticles (c) are all present (scale bars = 2 nm). Insets in the lower left corner are atomic models

Johnston-Peck et al. J. Phys.Chem.C. 2013, 117, 14463

TEM
at CFN



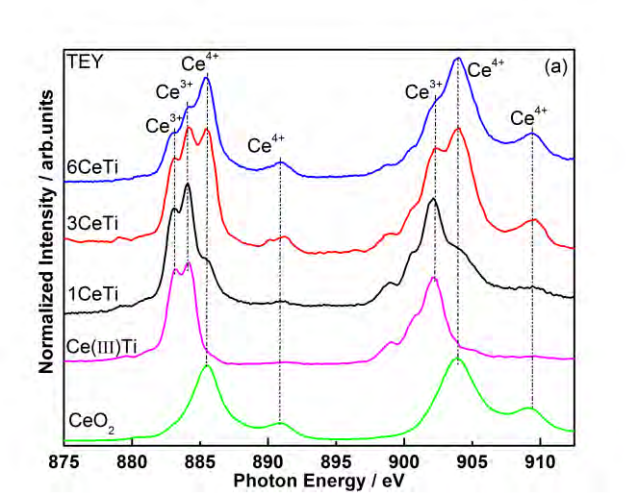
Ce^{3+} is present at the oxide-oxide interface

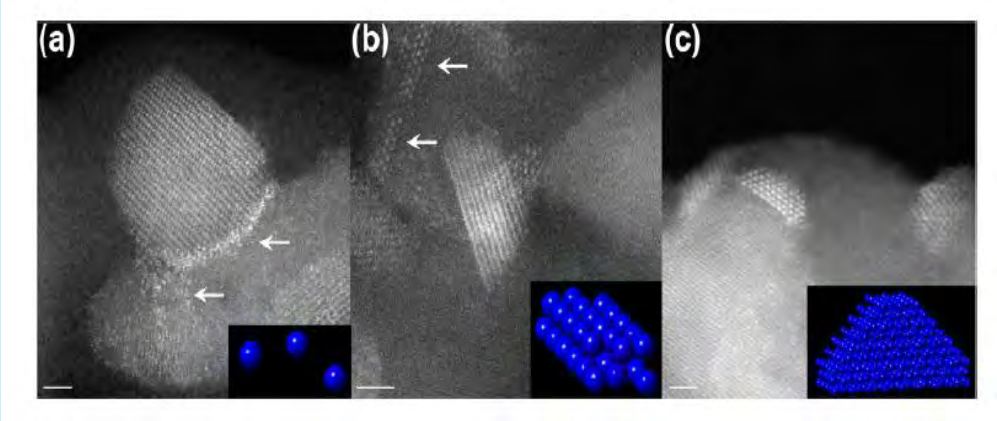
STEM-EELS spectra of a CeO_x/TiO_2 system. The particular ceria nanoparticle used for this measurement is depicted in the inset TEM image. The red line indicates the line along which the spectra were scanned for EELS signal.

Kundu et al. J. Phys.Chem.C. 2012, 116, 14062

NEXAFS

total electron yield

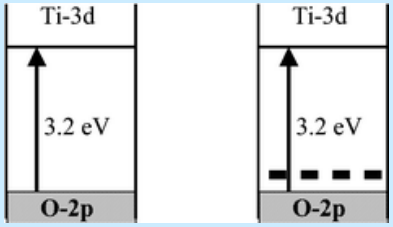




$1\%CeO_2/TiO_2$ $3\%CeO_2/TiO_2$ $6\%CeO_2/TiO_2$

concentration of Ce^{3+} :

bulk CeO_2 < $6\%CeO_2/TiO_2$ < $3\%CeO_2/TiO_2$ < $1\%CeO_2/TiO_2$

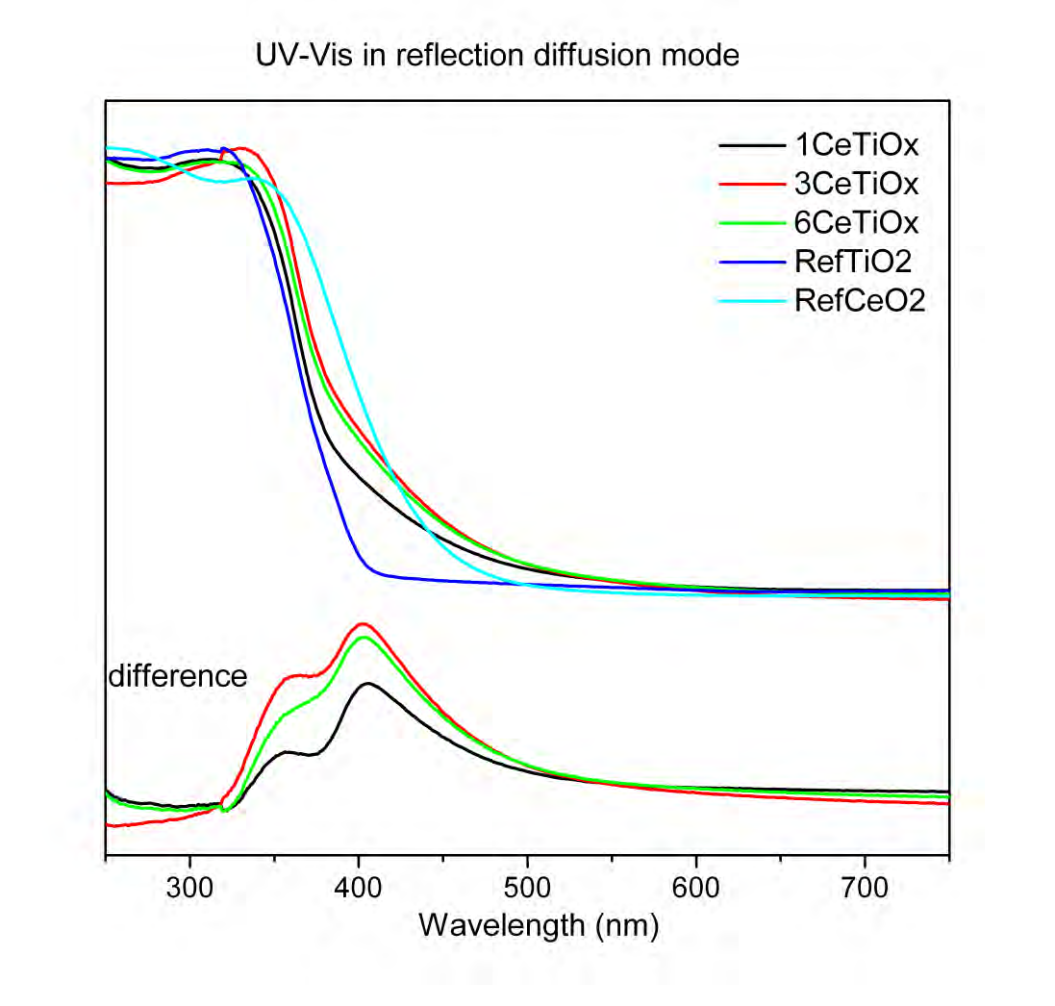


Ce 4f levels

Pure TiO_2

Mixed-metal oxide

Optical properties: UV-vis

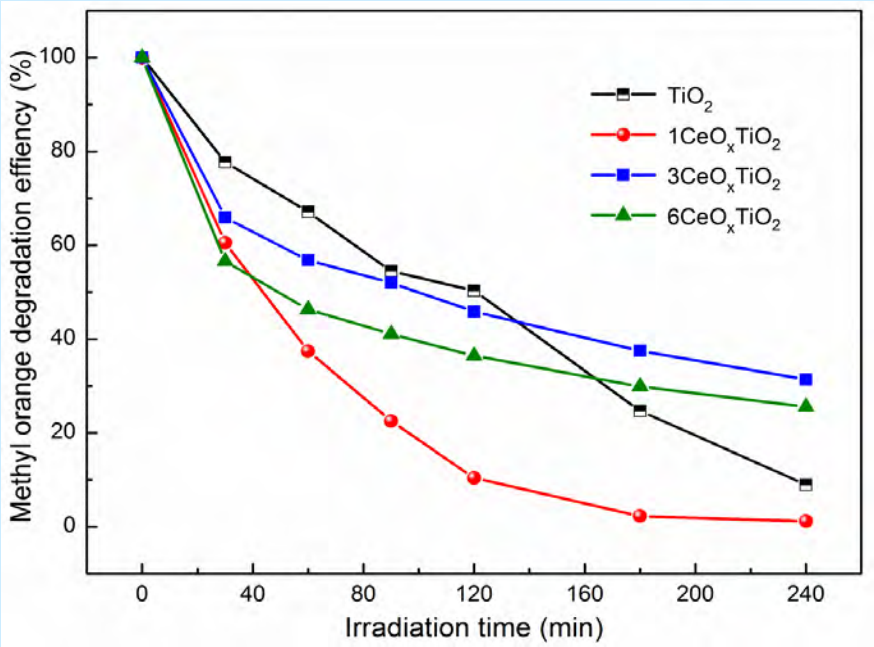


- The absorption of visible light is enhanced after the modification of ceria
- The enhancement is obvious when loading of ceria increases from 1% to 3%
- When ceria concentration increases from 3% to 6% the enhancement becomes minor

UV-Vis at CFN

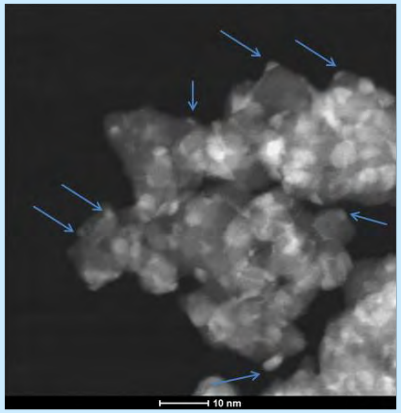
Photodegradation of methyl orange

UV illumination



CeO_x/TiO_2 → No active for water splitting

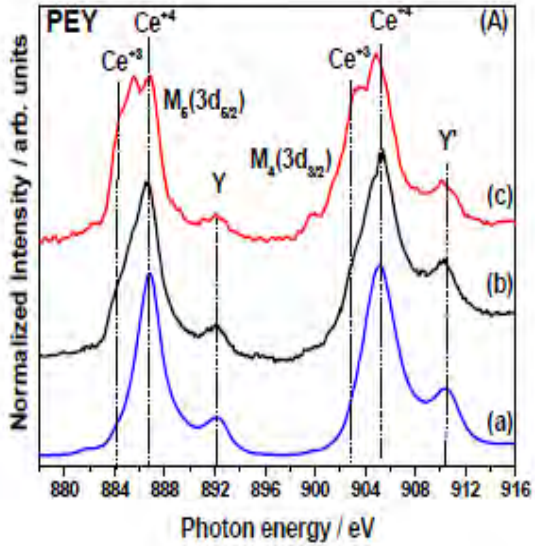
Pt + CeO_x/TiO_2 → Active for water splitting



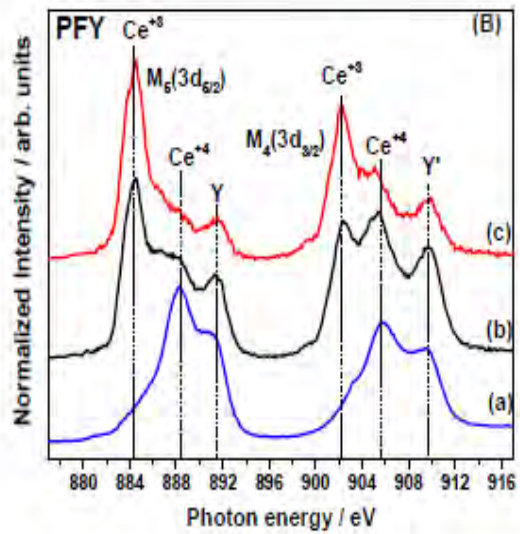
TEM of Pt/CeO_x/TiO_2

NEXAFS

partial electron yield



partial fluorescence yield



$Pt/CeO_2/TiO_2$

CeO_2/TiO_2

CeO_2

concentration of Ce^{3+} :

bulk CeO_2 < CeO_2/TiO_2 < $Pt/CeO_2/TiO_2$

NSLS U4A

Kundu et al. J. Phys.Chem.C. 2012, 116, 14062

Photocatalytic splitting of water

UV-vis
at CFN

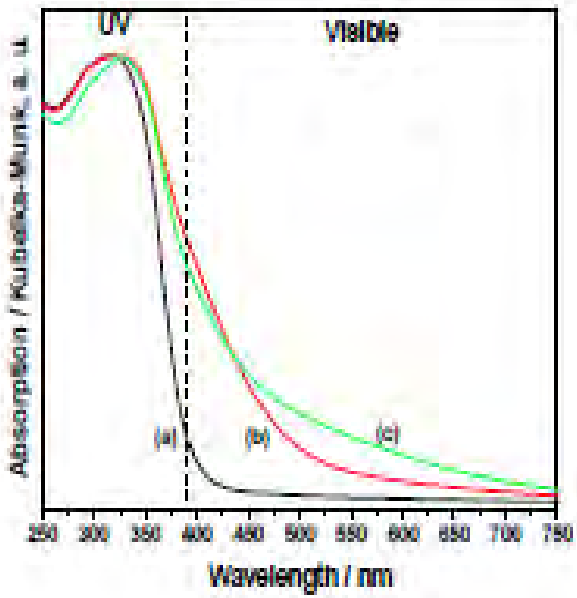


Figure 3. UV–Vis spectra obtained in diffuse reflection mode for (a) pure TiO_2, (b) 15 wt% CeO_2 dispersed on TiO_2 and (c) 0.5wt% of Pt loaded on 15 wt% CeO_2/ TiO_2 support.

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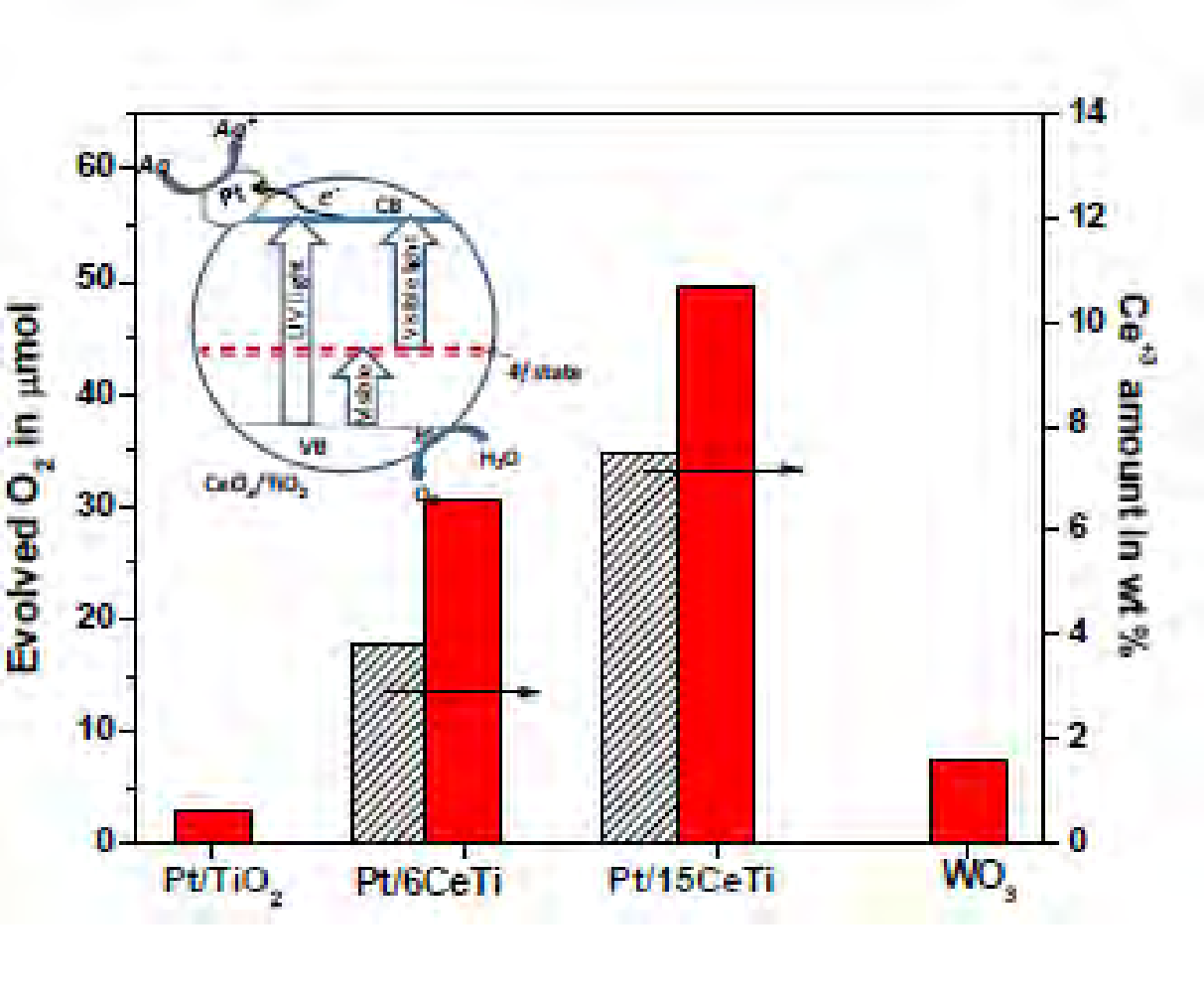
Photocatalytic splitting of water



Pt/CeO_x/TiO_2 better photocatalyst than WO_3 standard.

Correlation between photocatalytic activity and concentration of Ce^{3+} in the interface

The left axis and red bars show the amount of oxygen evolved on Pt/TiO_2, Pt/CeO_2/TiO_2 and WO_3 catalysts from water photo-oxidation upon visible light (λ >400nm) illumination for 4 hours. The right axis displays the amount of Ce^{+3} present in the Pt/CeO_2/TiO_2 catalysts calculated from the corresponding Ce M-edge NEXAFS spectra obtained by PEY measurements.

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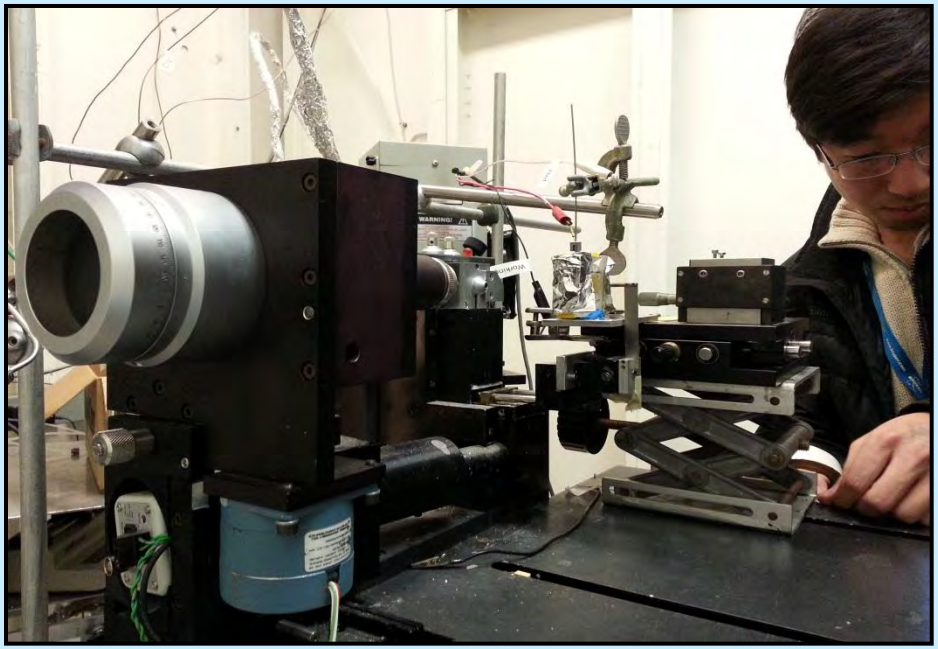
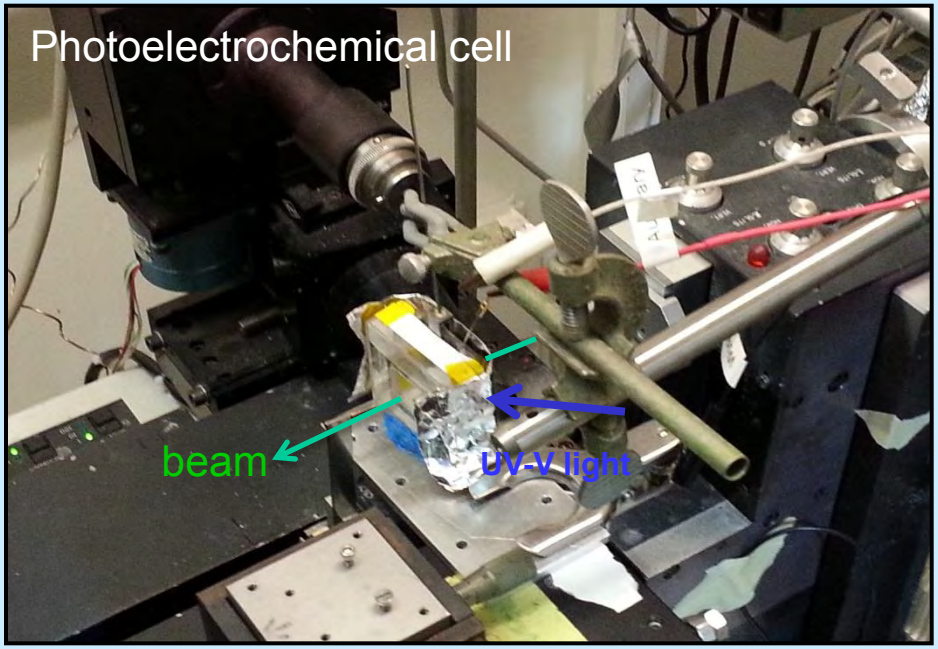
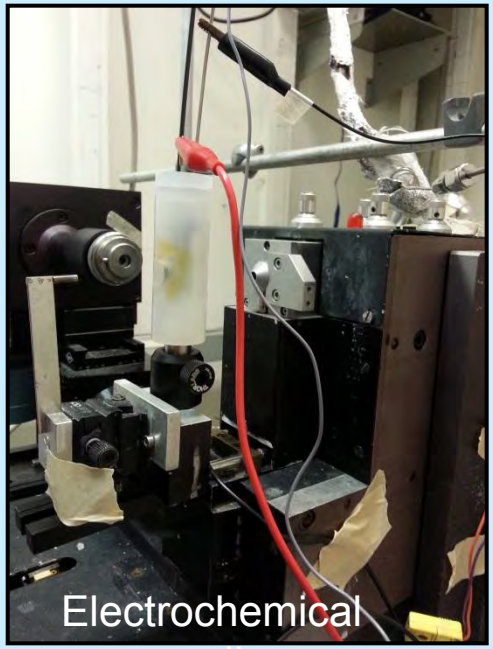
Future *in-situ* studies taking advantage of time-resolved X-ray diffraction







***In situ* XRD on PEC cell @ beamline X7B**

Working electrode

Summary

- The deposition of CeO_x nanoparticles on TiO_2 proves to be an efficient way to modify the chemical and electronic properties of both metal oxides as observed from NEXAFS, XPS and UV–Vis measurements.

- Although Ce_2O_3 is not a stable oxide, our study shows that it is possible to stabilize Ce^{+3} cations within a mixed oxide interface, which then can absorb photons in the visible region.

- $Pt/CeO_x/TiO_2$ proved to be excellent for the photocatalytic splitting of water in the visible region being about seven times more active than a WO_3 standard.

- Photocatalysts can be designed taking advantage of the special interactions that occur in a mixed-metal oxide at the nanometer level. The NSLS II will offer unique tools for the characterization of these complex materials.