Challenging nanomaterials for sustainable processes

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Department of Chemical and Pharmaceutical Sciences
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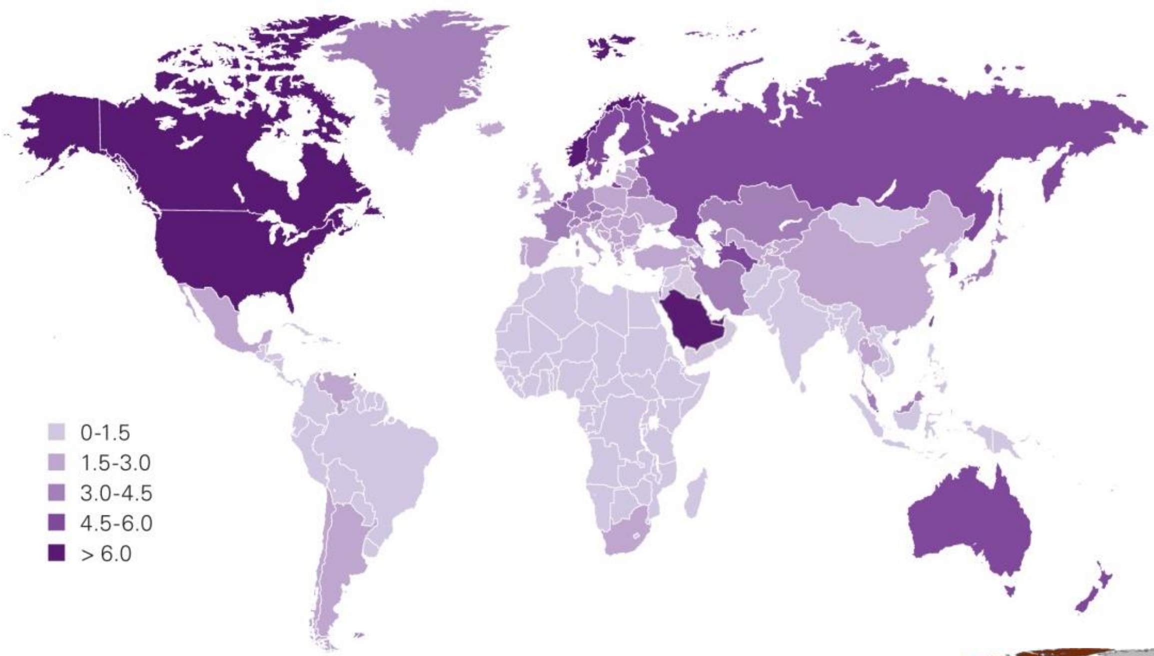
"Nanotechnology and NanoApplication"
Ljubljana, 5 February 2020

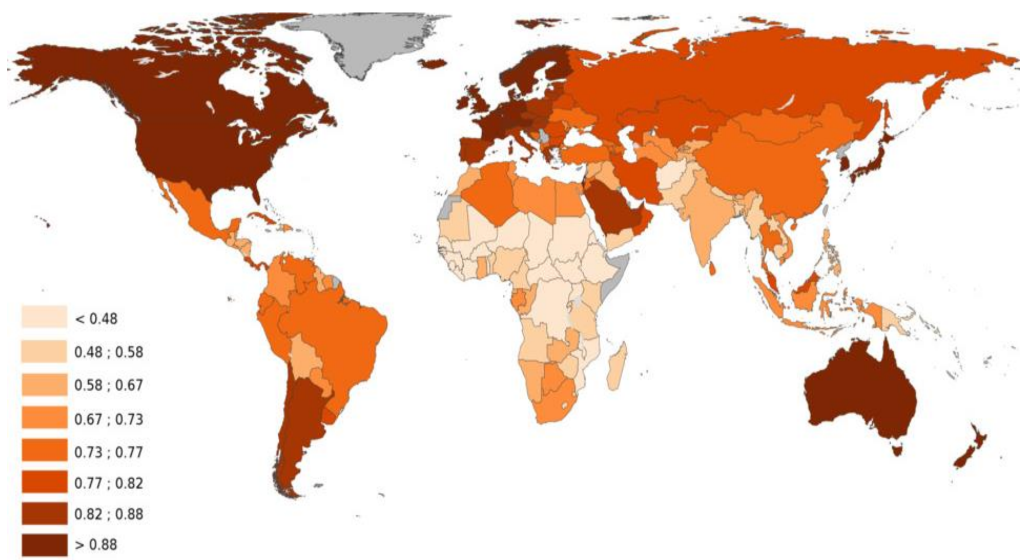
ENERGY CONSUMPTION VS POPULATION



Primary Energy Consumption per Capita

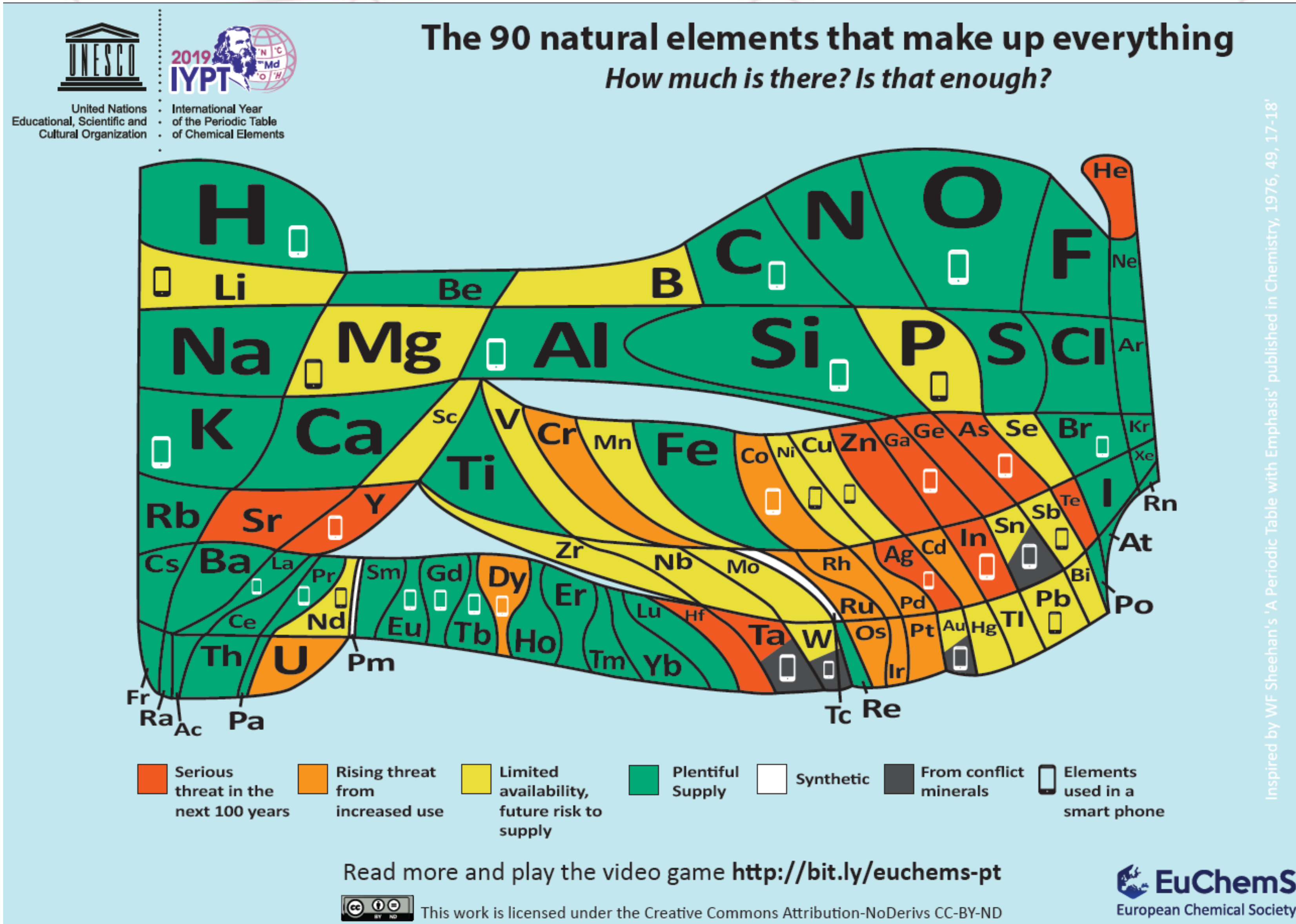
Tonns of oil equivalent

Human Development Index



BP Statistical Review of Wolrd Enery 2016

DEPLETION

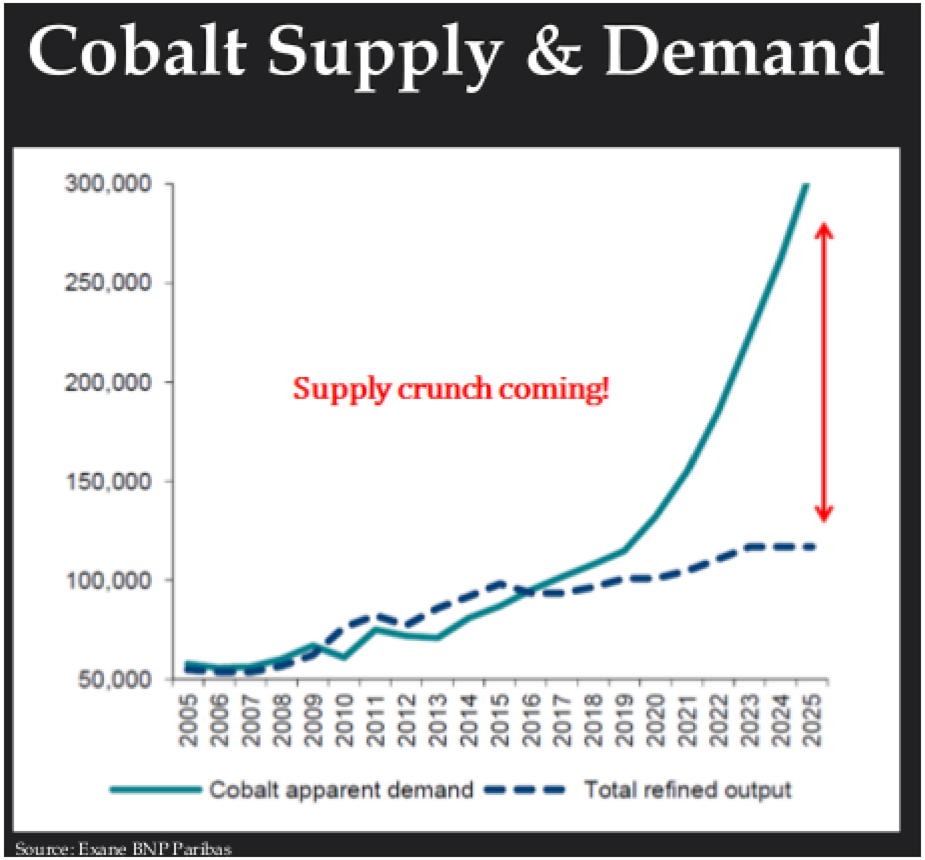


United Nations Educational, Scientific and Cultural Organization
2019 IYPT
International Year of the Periodic Table of Chemical Elements
The 90 natural elements that make up everything
How much is there? Is that enough?
H He Li Be B C N O F Ne Na Mg Al Si P S Cl Ar K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe Cs Ba La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn Fr Ra Ac Th Pa U
Serious threat in the next 100 years
Rising threat from increased use
Limited availability, future risk to supply
Plentiful Supply
Synthetic
From conflict minerals
Elements used in a smart phone
Inspired by WF Sheehan's 'A Periodic Table with Emphasis' published in Chemistry, 1976, 49, 17-18'
Read more and play the video game http://bit.ly/euchems-pt
This work is licensed under the Creative Commons Attribution-NoDerivs CC-BY-ND
EuChemS
European Chemical Society

DEPLETION

The famous Carlin-type gold ores of Nevada are often found in limestone or lime-rich shales. Tens of millions of ounces of gold have been mined from rocks just like this.

ETHICAL COBALT EXTRACTION



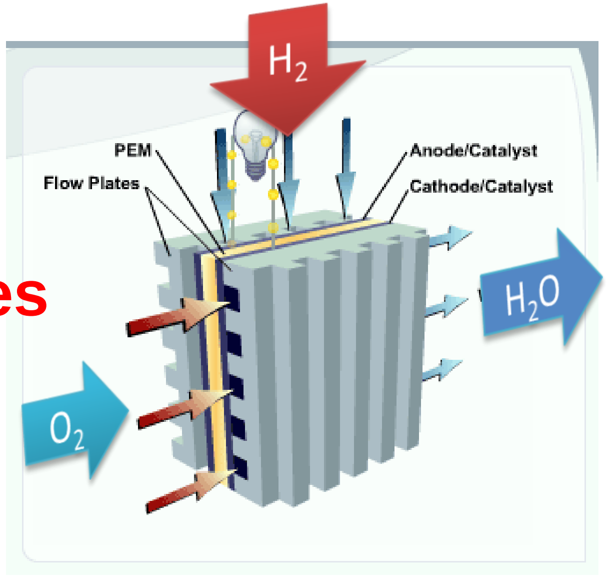
Replacing noble metals with base metal (?)

To sustainable satisfy population needs

Extensive use of renewable energy sources and raw materials

More efficient processes for production of energy and chemicals

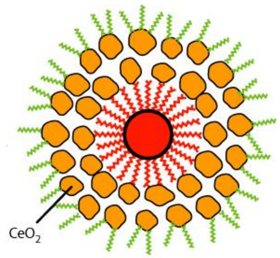
Design of new catalytic materials with improved properties for new sustainable processes



MEE RESEARCH ACTIVITIES

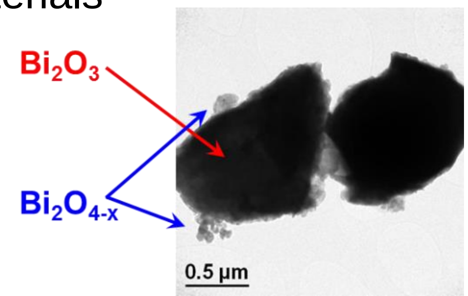
Air pollution abatement

- Three Way Catalysts
- CH_4 combustion



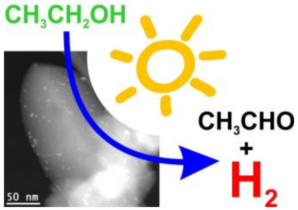
Water purification by photocatalysis

- Doped TiO_2
- Bi_2O_3-based materials
- Metal tungstates



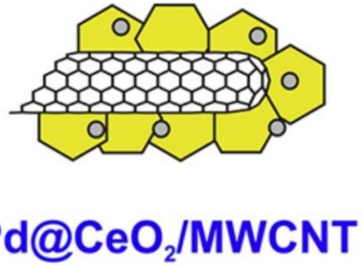
H_2 & Fuels production

- CH_4 partial oxidation
- Steam reforming of renewable compounds
- Photocatalytic reforming of oxygenated compounds
- Synthesis of valuable organic compounds



H_2 purification

- Water Gas Shift
- Preferential Oxidation of CO



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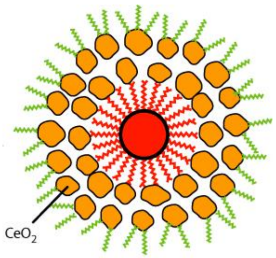

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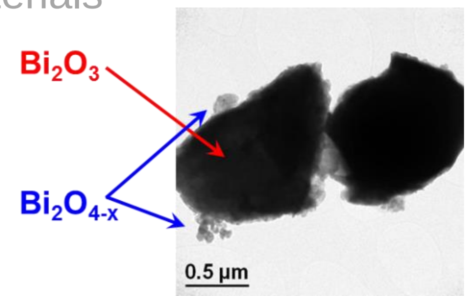

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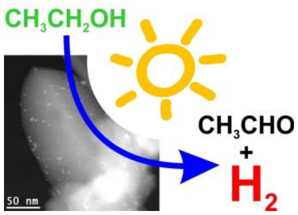

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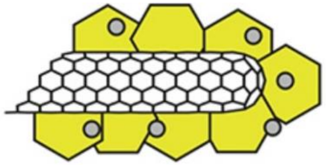
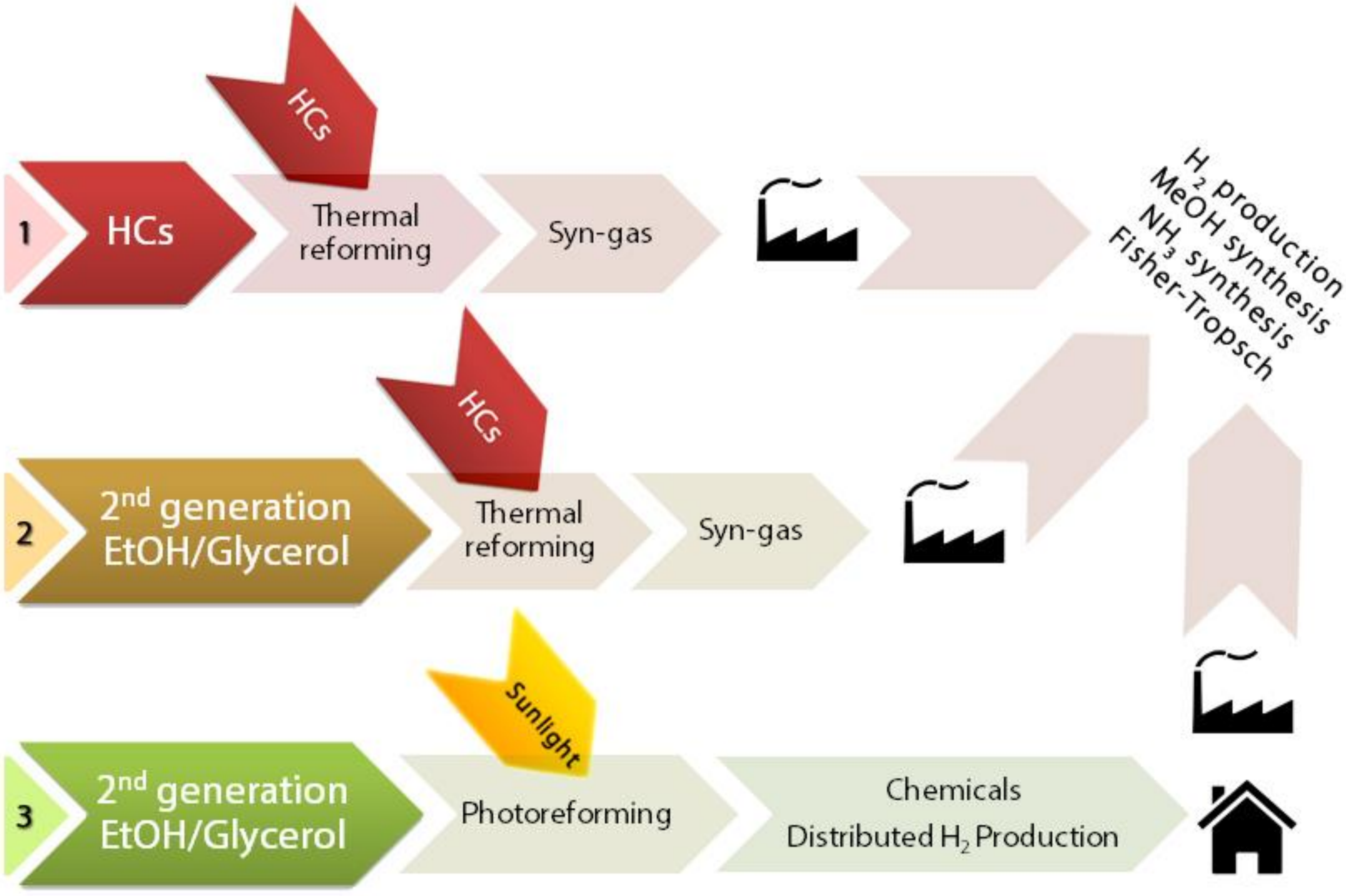
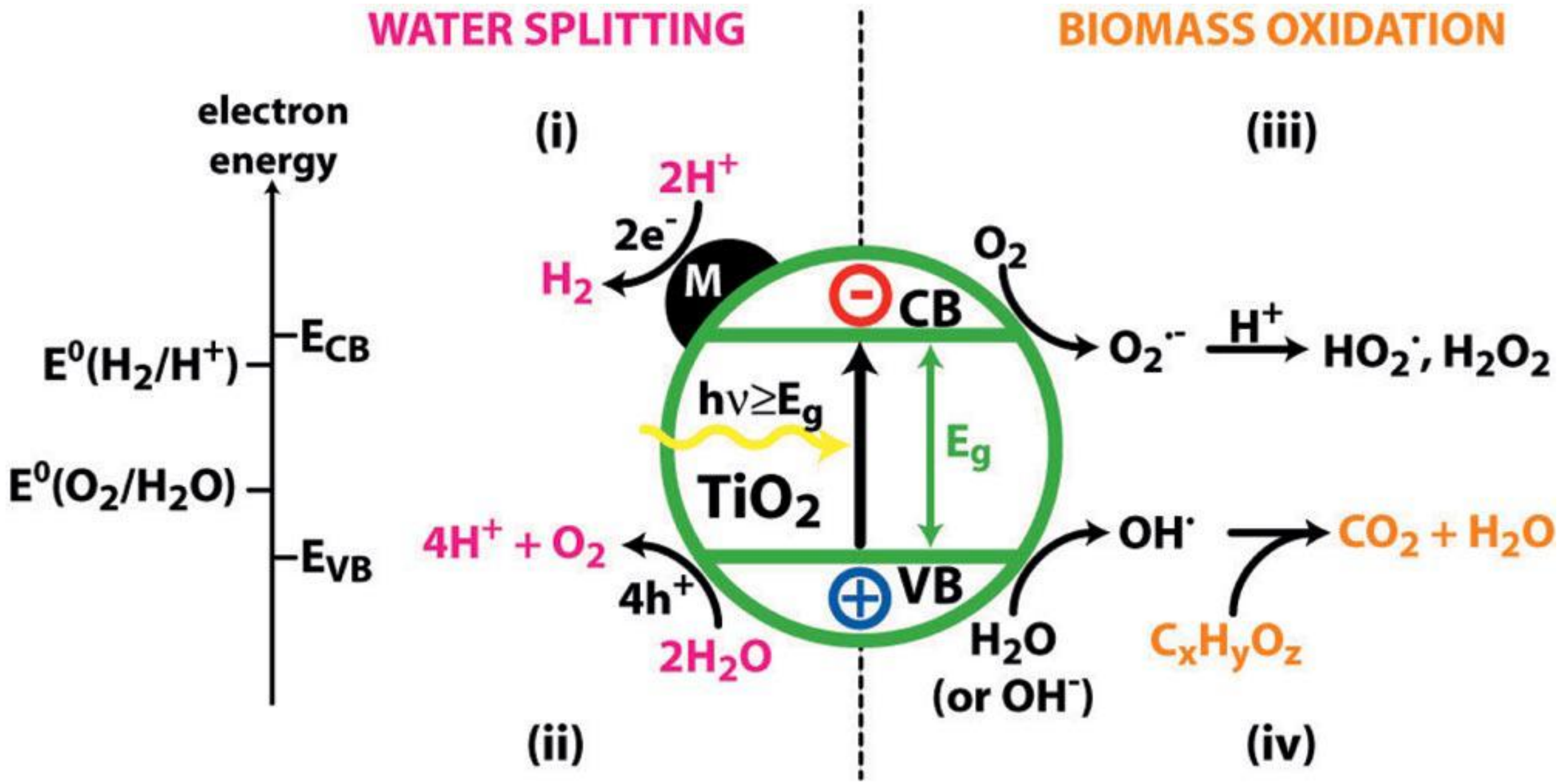


H_2 PRODUCTION TECHNOLOGIES



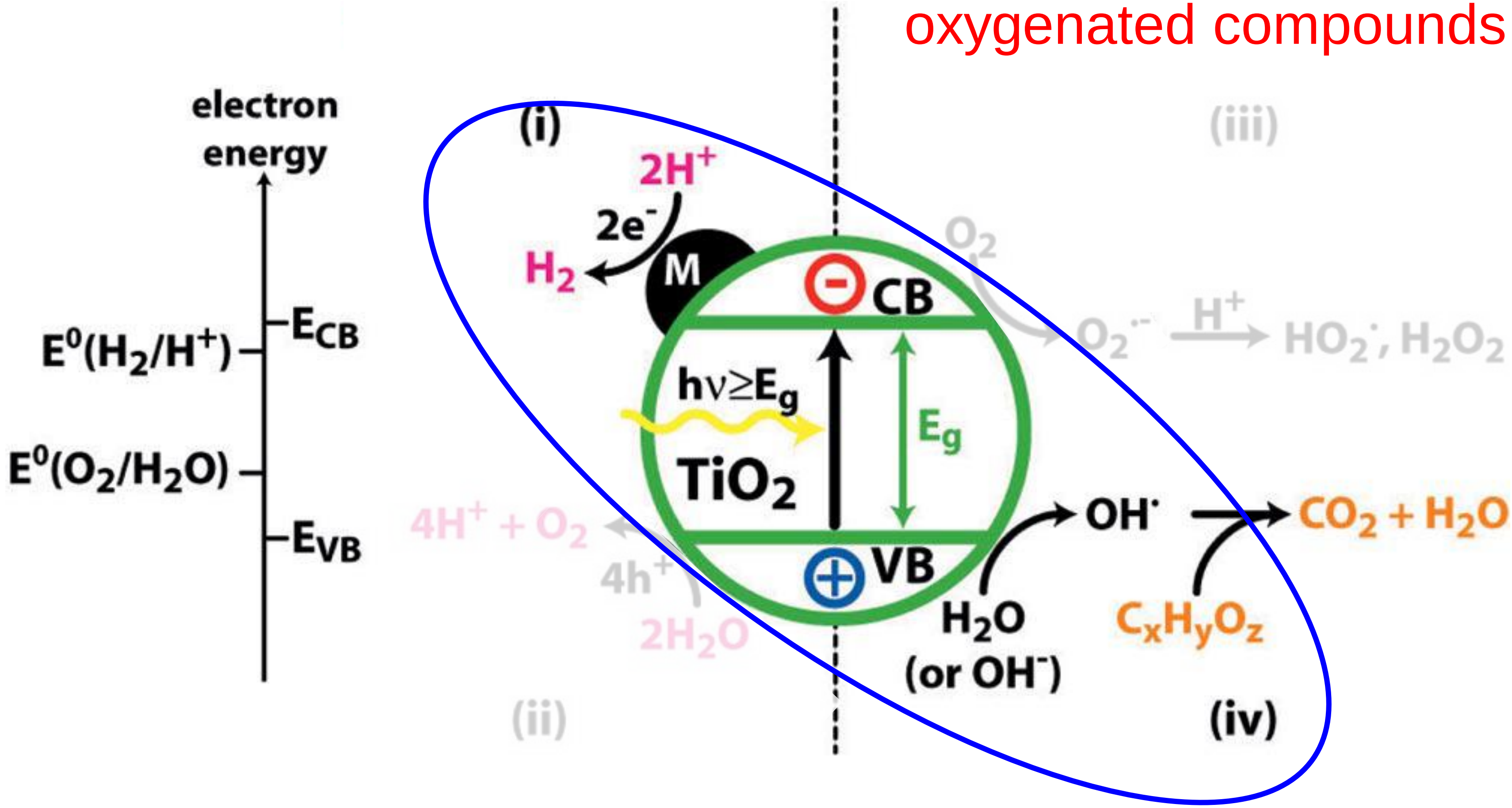
Mater. Sci. Semicond. Process. **42** (2016) 122-130

PHOTOCATALYTIC H_2 PRODUCTION



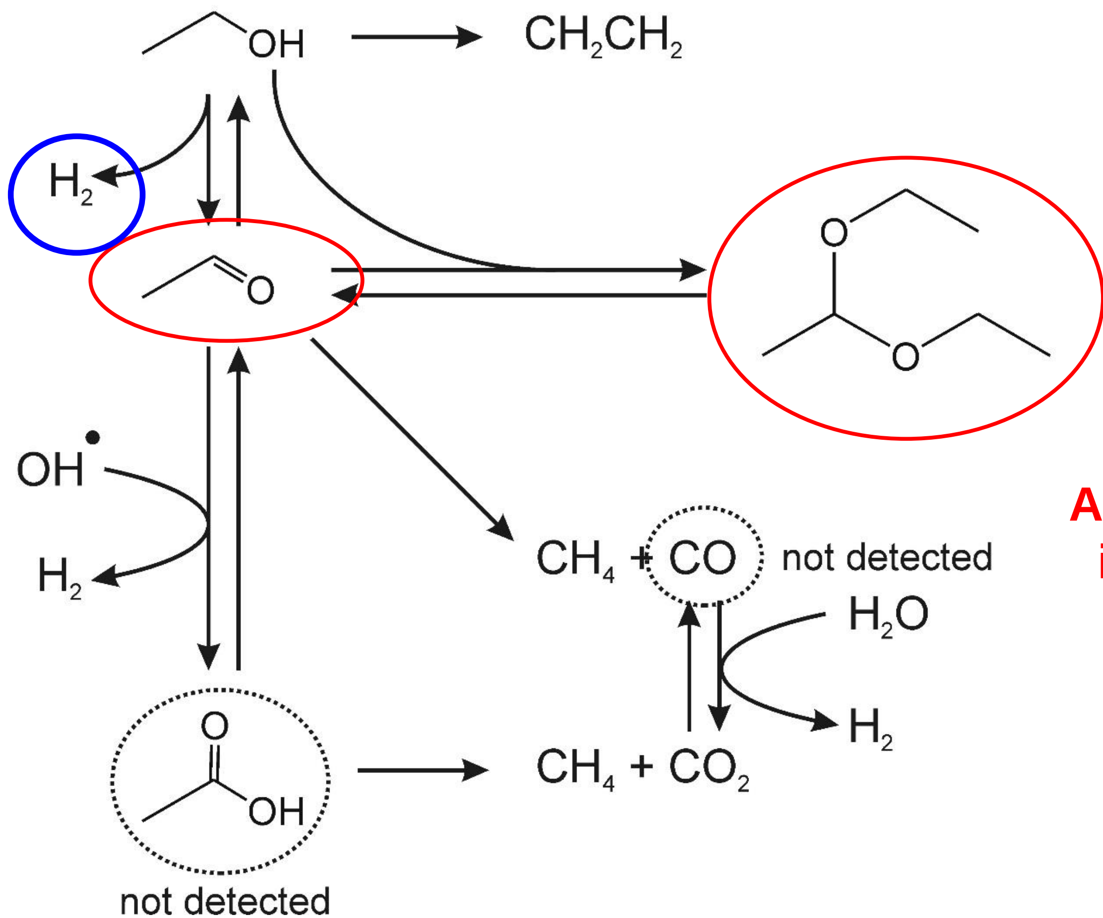
Eur. J. Inorg. Chem. **2011** (2011), 4309-4323

Photoreforming of oxygenated compounds



Eur. J. Inorg. Chem. **2011** (2011), 4309-4323

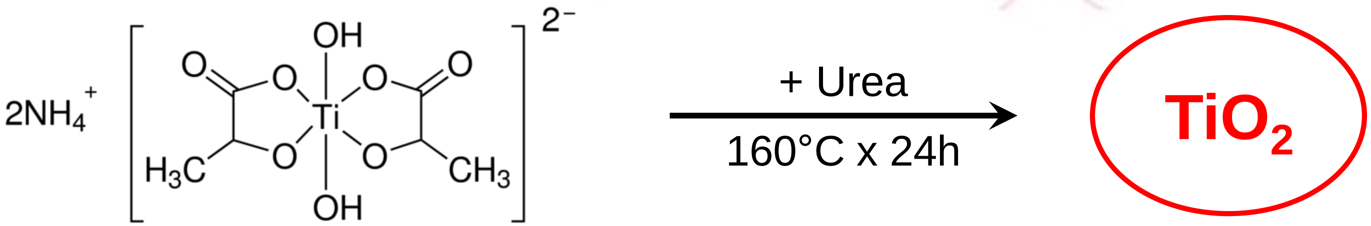
Possible pathway



Accumulated in solution

ChemCatChem **3** (2011), 574-577

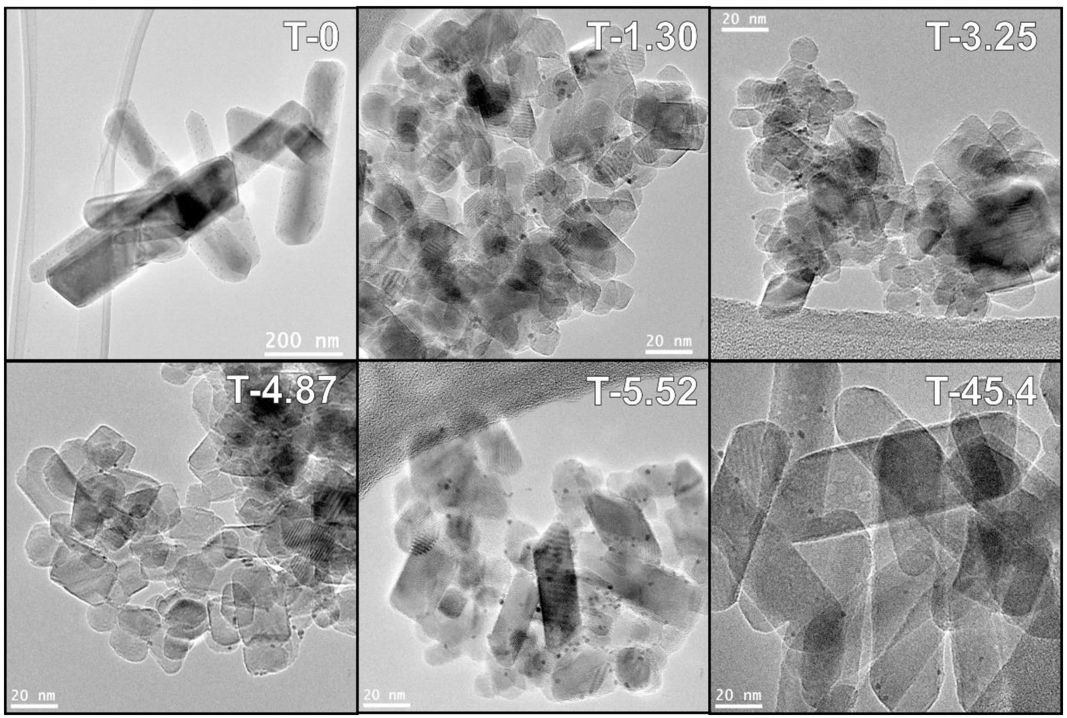
TUNING TiO_2 COMPOSITION



R + A

Rutile

Anatase



A + B

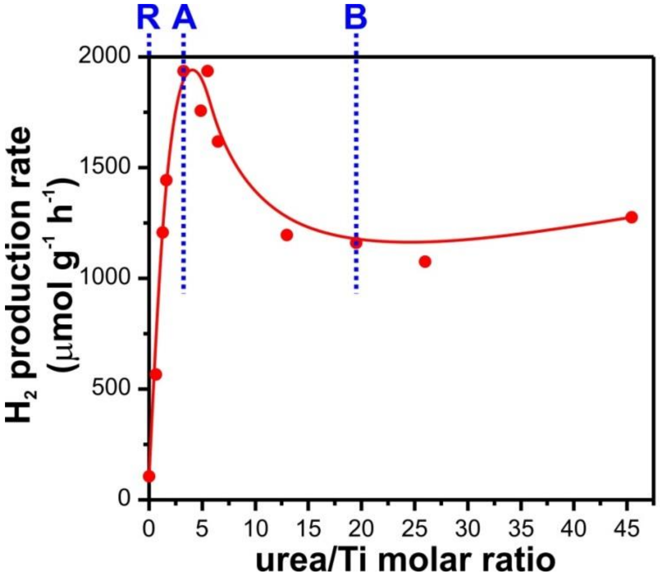
A + B

Brookite

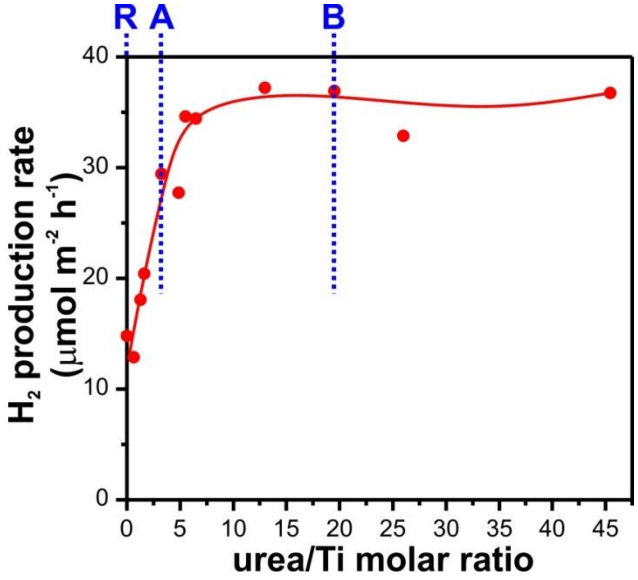
Appl. Catal. A-Gen. **518** (2016), 167-175

TUNING TiO_2 COMPOSITION

Per mass



Per surface area

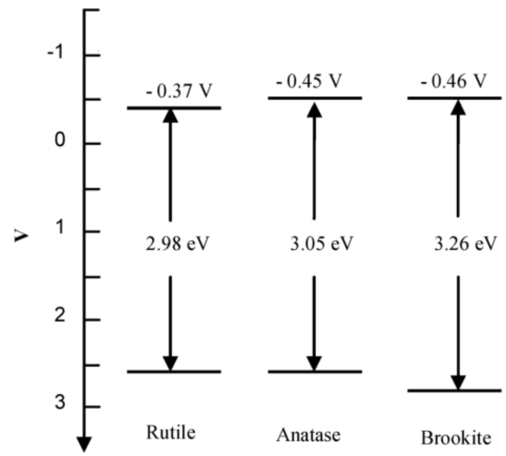


Ethanol/water solution
Simulated sunlight

Pt 0.2 wt% added as co-catalysts

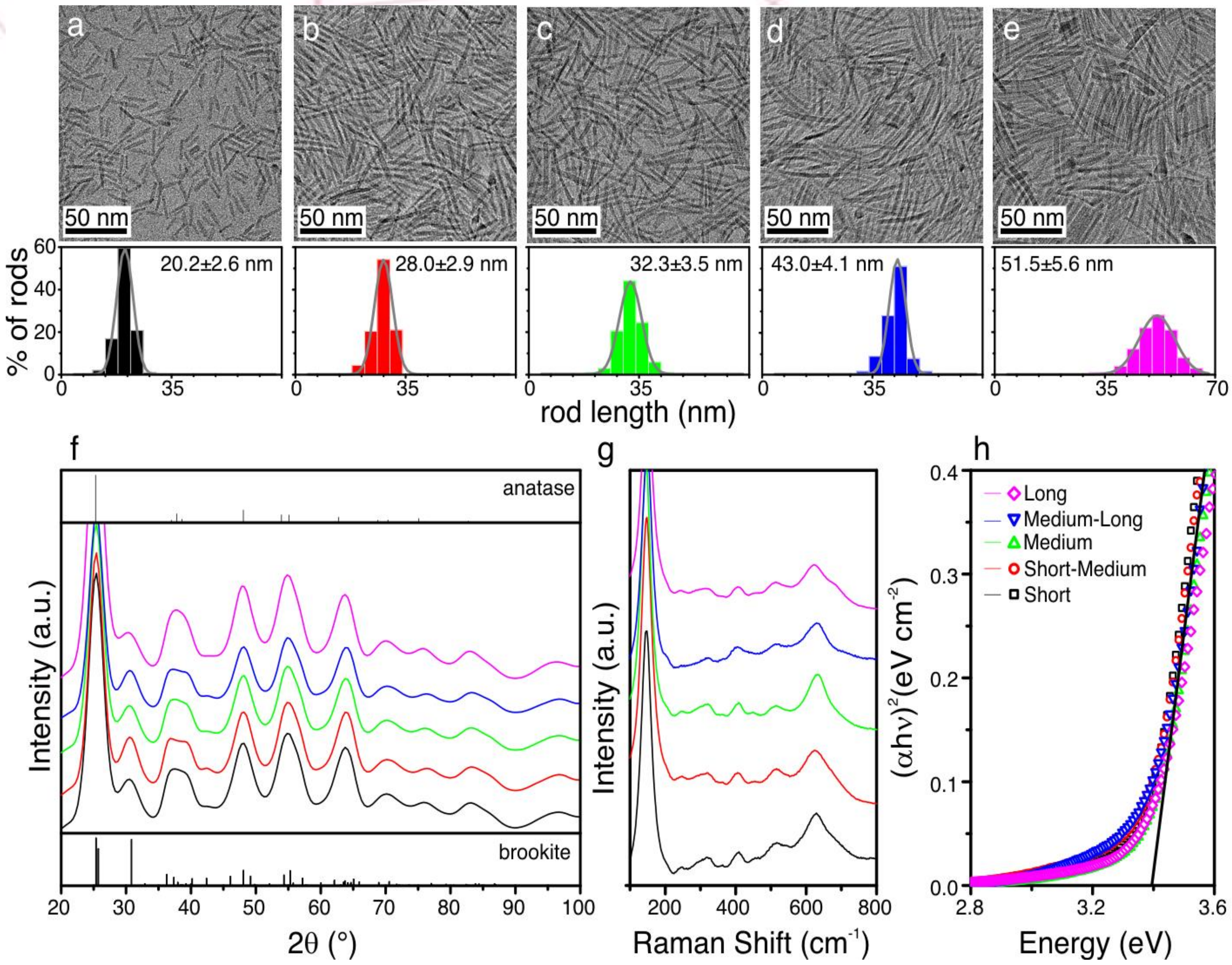
Brookite:

- Favorable electronic properties
- Well defined morphology and exposed facets



Appl. Catal. A-Gen. **518** (2016), 167-175

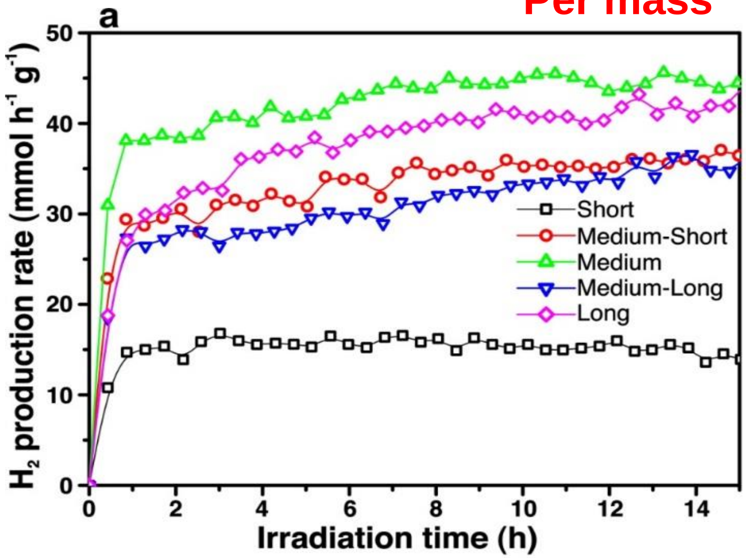
TiO_2 BROOKITE NANORODS



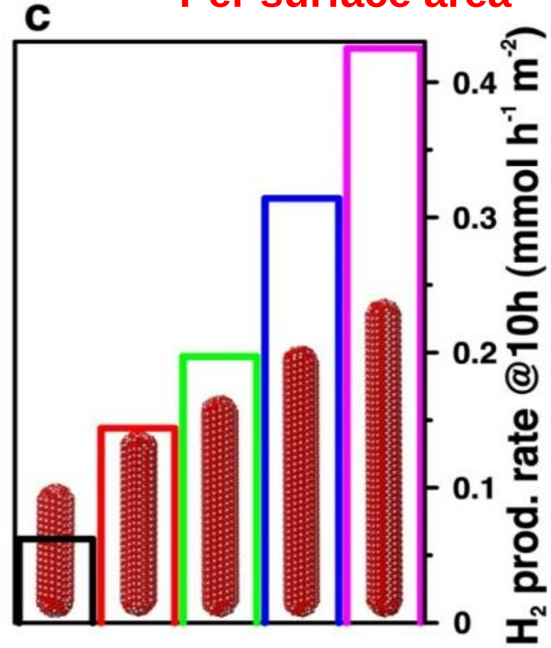
Proc. Nat. Acad. Sci., **113** (2016), 3966-3971

TiO_2 BROOKITE NANORODS

Per mass



Per surface area

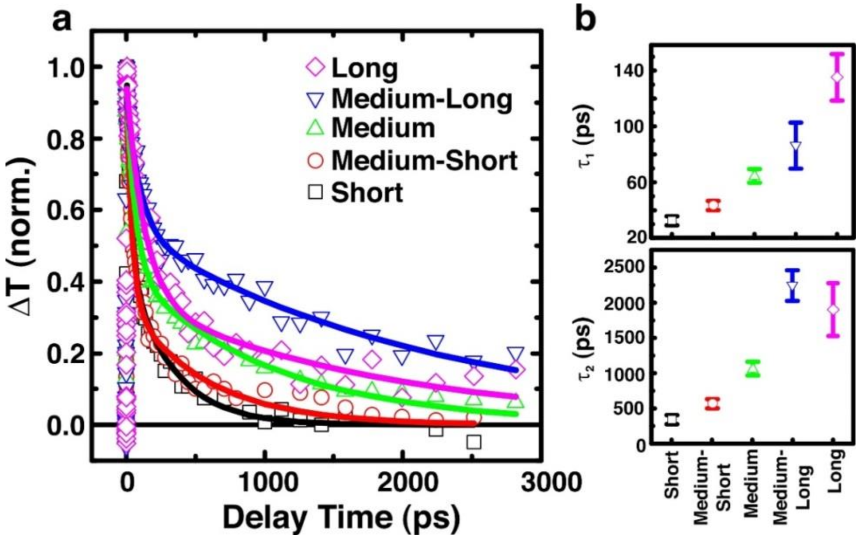


Proc. Nat. Acad. Sci., **113** (2016), 3966-3971

TiO_2 BROOKITE NANORODS

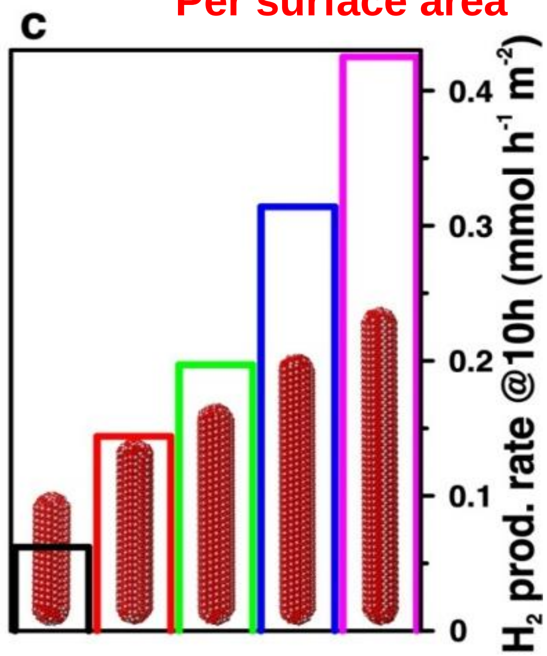
50 fs ultraviolet (4.0 eV) pump pulse

$$\frac{\Delta T}{|\Delta T_{MAX}|} = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}}$$



- Increase life-time of electron/hole pairs with length

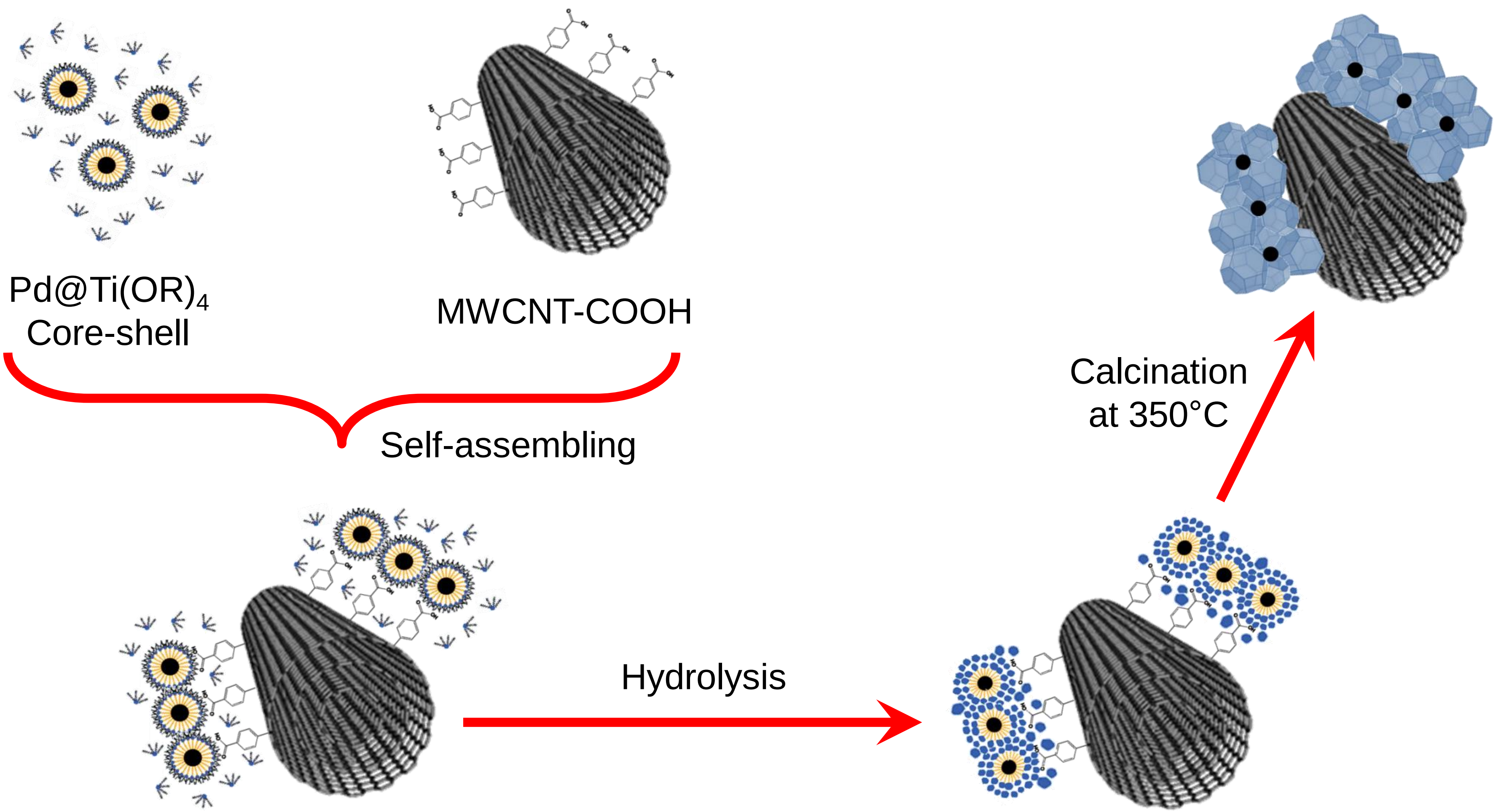
Per surface area



Proc. Nat. Acad. Sci., **113** (2016), 3966-3971

Pd@TiO$_2$/CARBON NANOTUBES

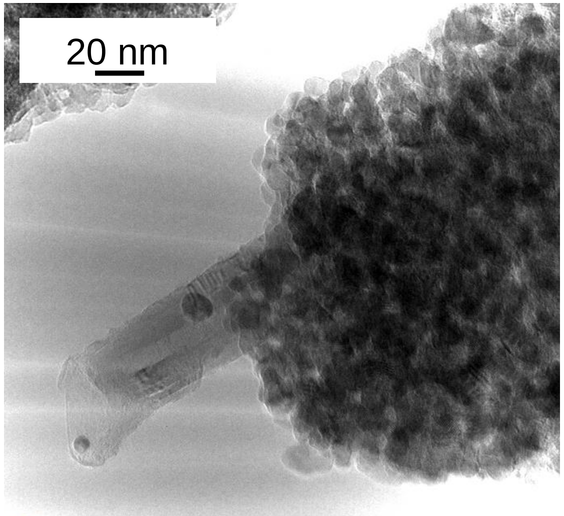
Formation of hybrid materials

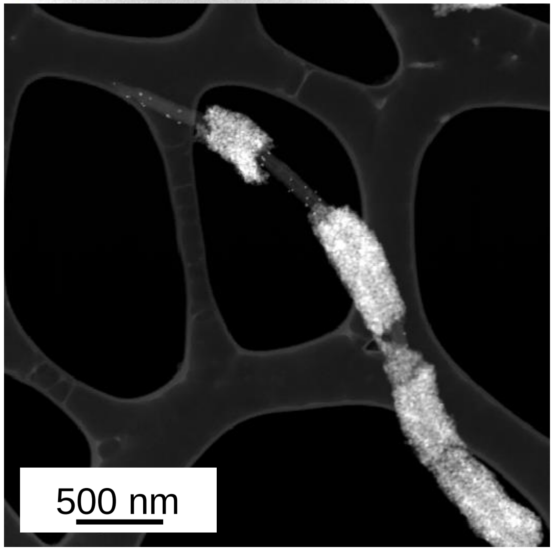


Green Chem. **19** (2017), 2379-2389

Pd@TiO_2/CARBON NANOTUBES

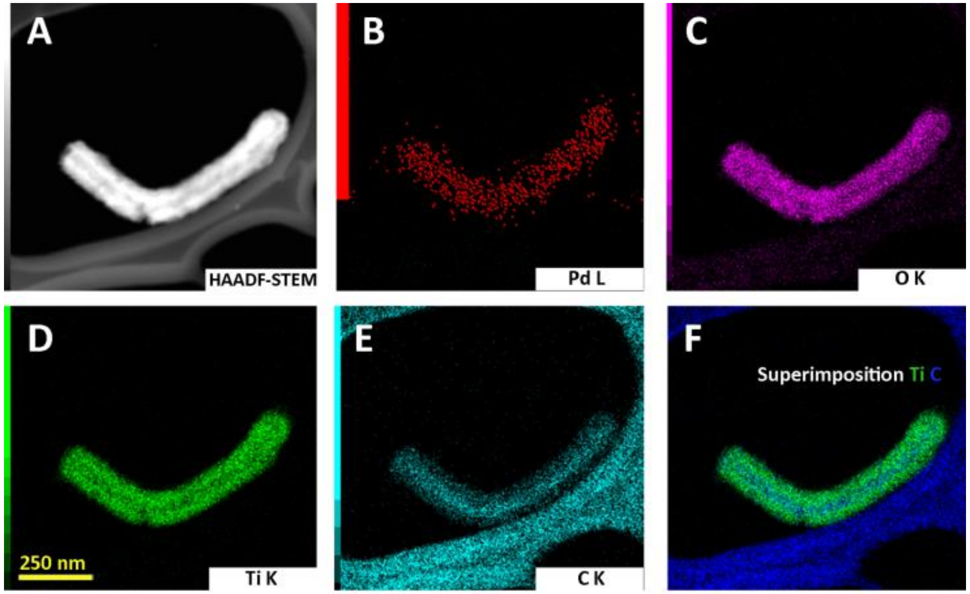
After calcination





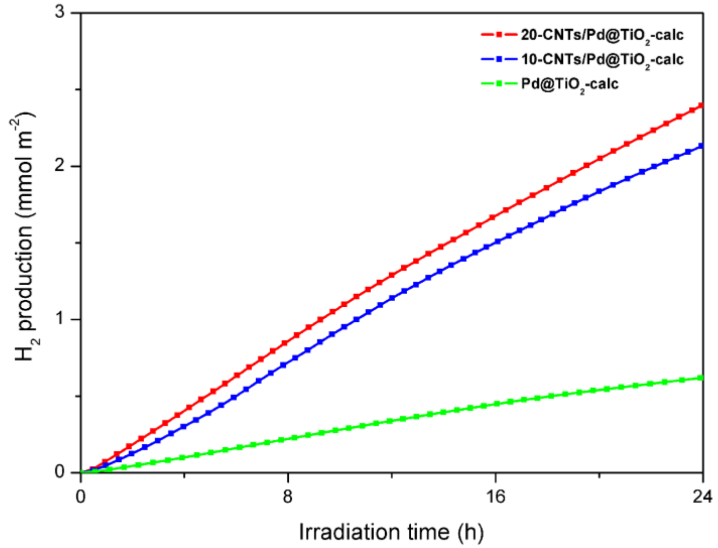
- Porous Pd@TiO_2 shell around CNT
- Anatase phase

EF-TEM

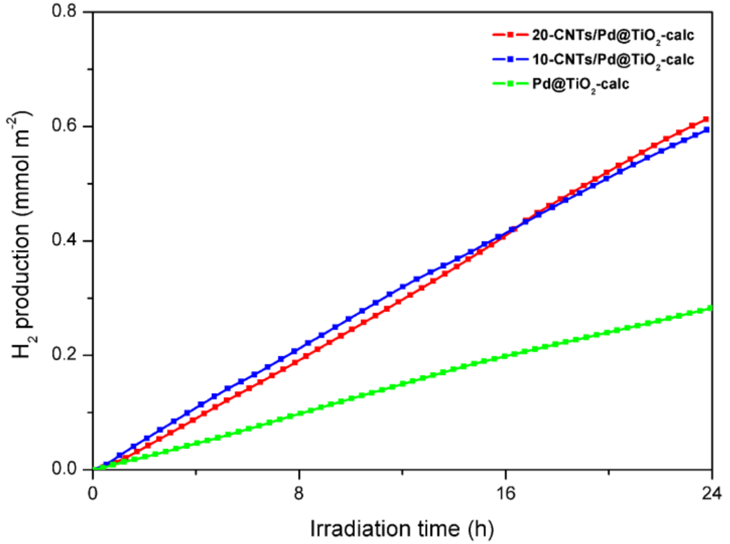


Green Chem. **19** (2017), 2379-2389

Pd@TiO_2/CARBON NANOTUBES



Ethanol/water solution

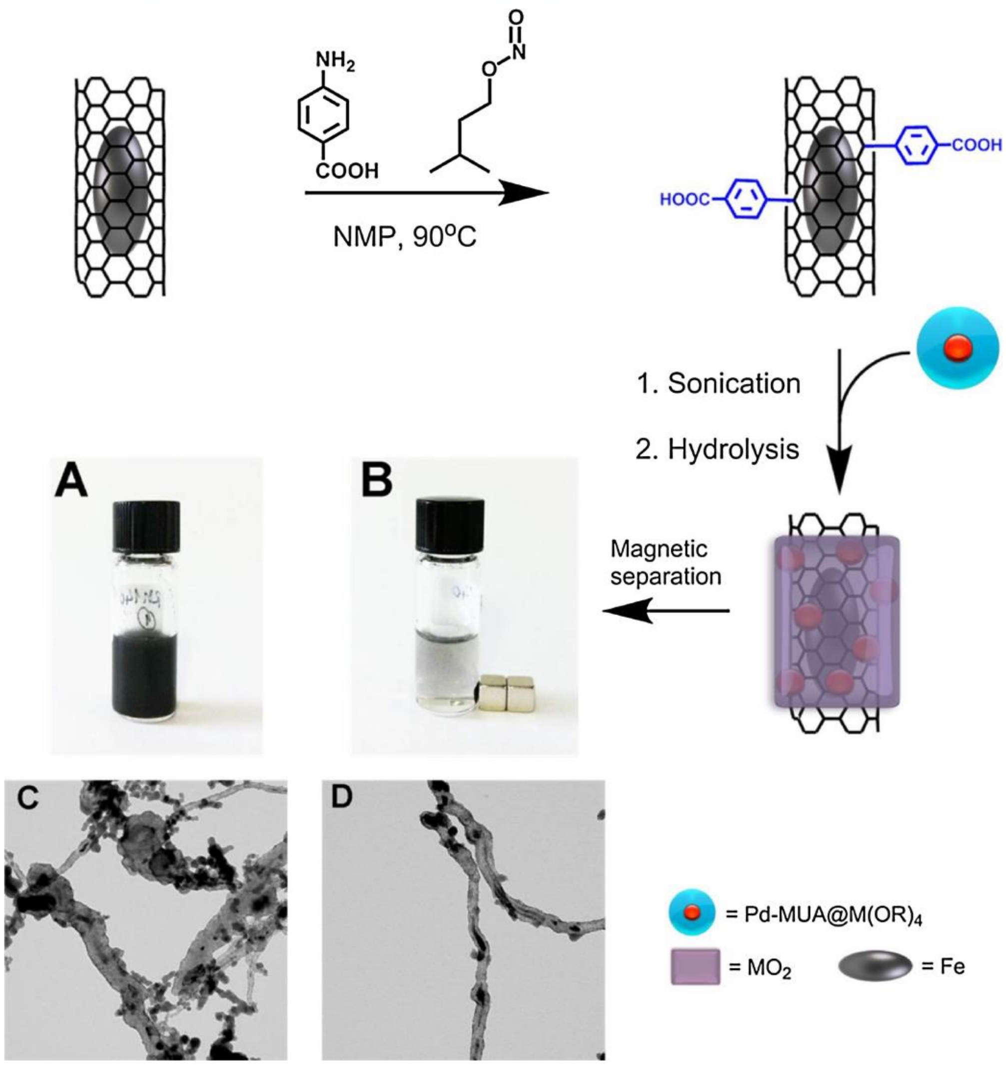


Glycerol/water solution

H_2 production under UV-vis irradiation

Green Chem. **19** (2017), 2379-2389

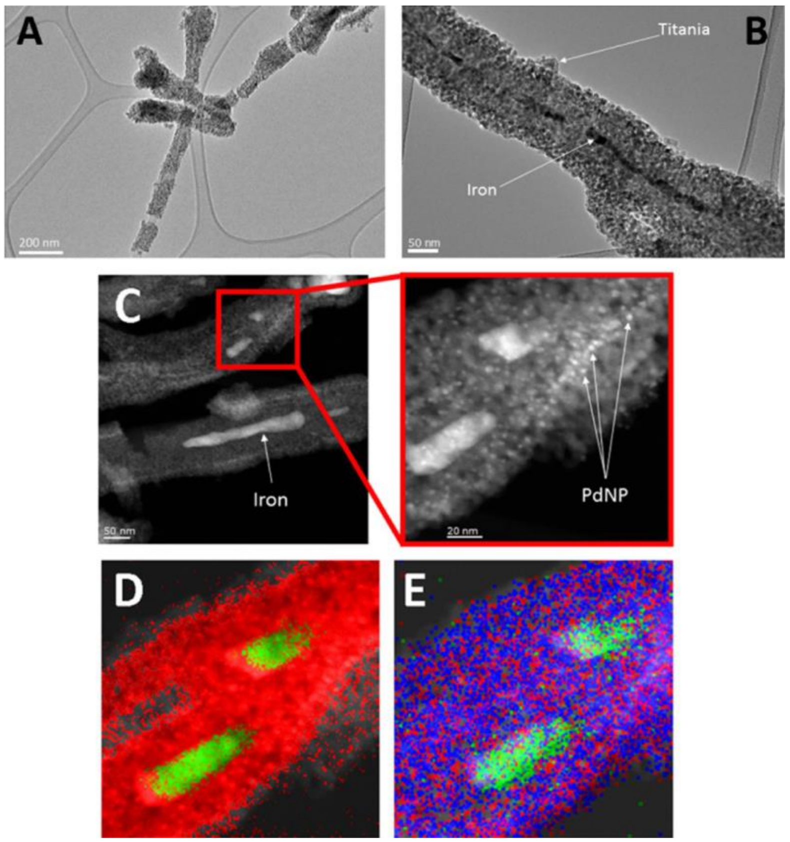
Pd@TiO$_2$/CARBON NANOTUBES@Fe



Before

After

Purification by magnetic separation

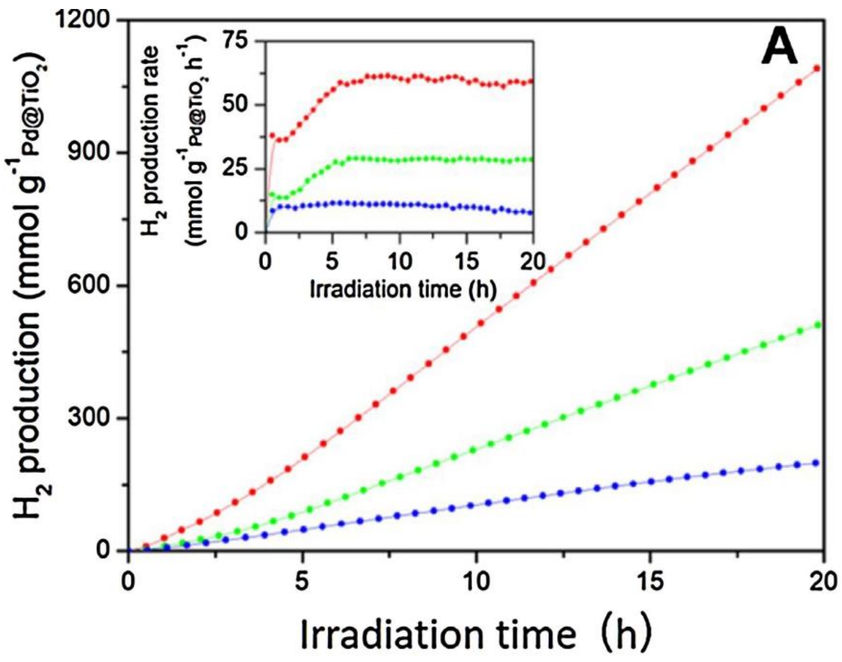


Appl. Catal. B-Environ. **227** *(2018), 356-365*

Pd@TiO$_2$/CARBON NANOTUBES@Fe

EtOH : H_2O = 1:1

UV-vis irradiation



Pd@TiO$_2$/Fe@CNT-magnetic

Pd@TiO$_2$/Fe@CNT-filtered

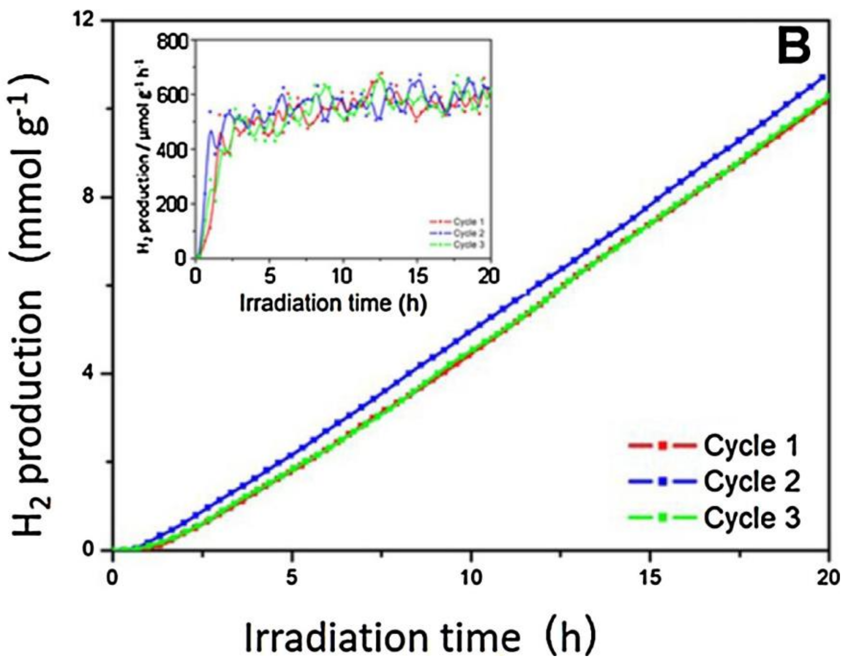
Pd@TiO$_2$

Appl. Catal. B-Environ. **227** *(2018), 356-365*

Pd@TiO$_2$/CARBON NANOTUBES@Fe

EtOH : H_2O = 1:1
Simulated Sunlight irradiation

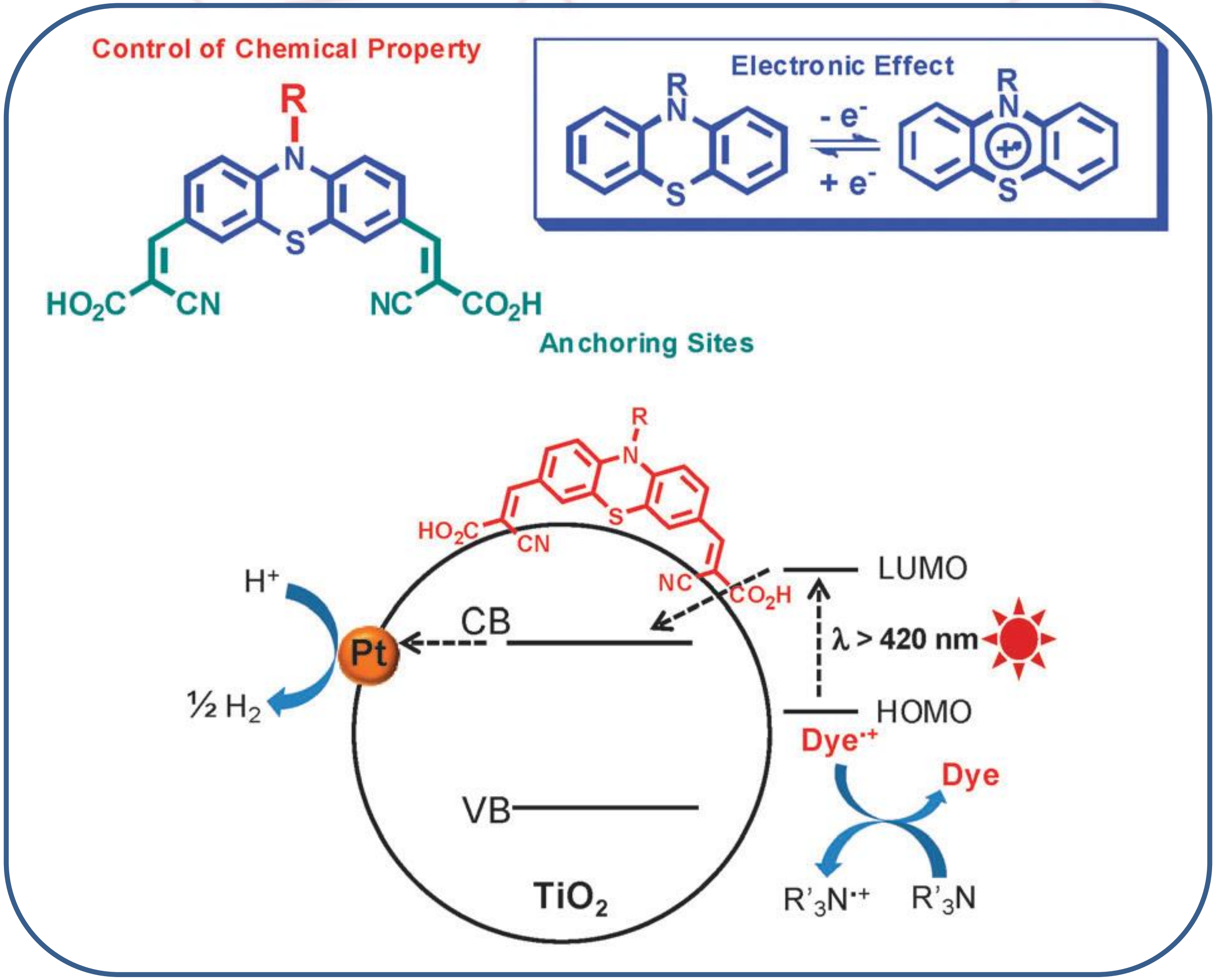
Pd@TiO$_2$/Fe@CNT-magnetic



Easily reusable by magnetic recovery from the reaction mixture!!!

Appl. Catal. B-Environ. **227** *(2018), 356-365*

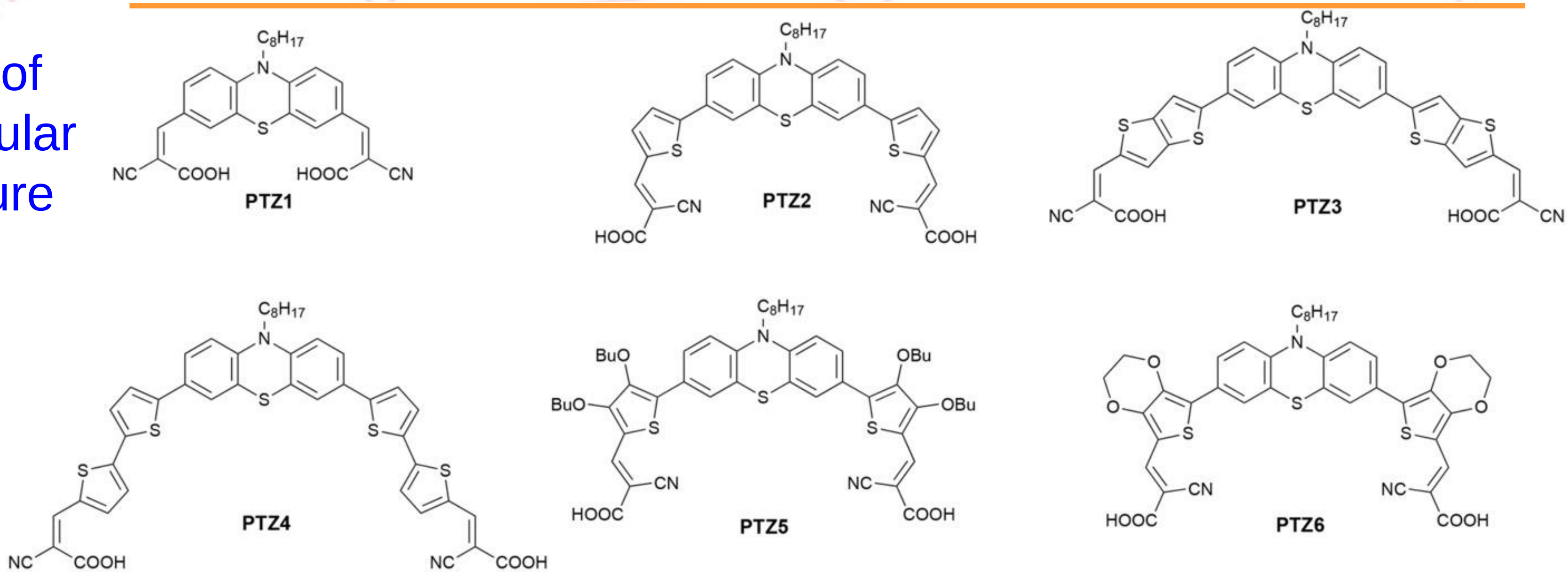
DYE SENSITIZED PHOTOCATALYSTS



✓ Materials active under visible light (λ > 420nm)

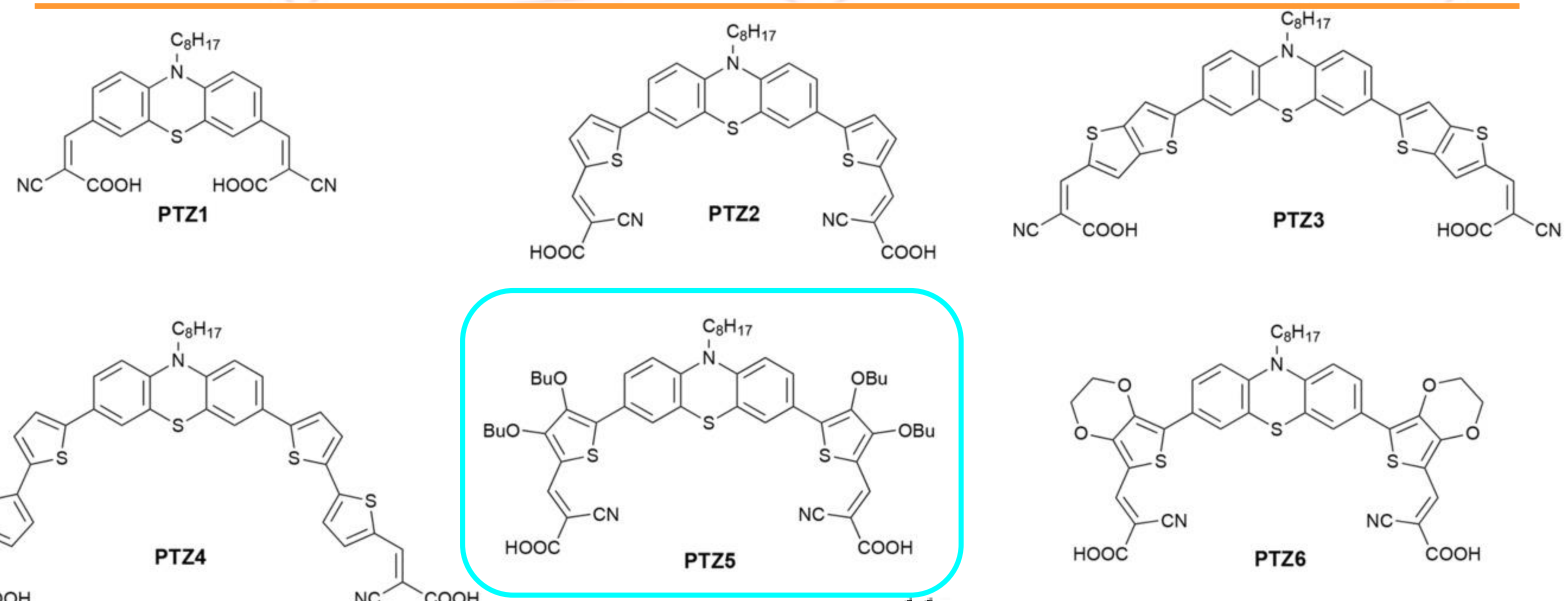
x Not sustainable Sacrificial Electron Donor

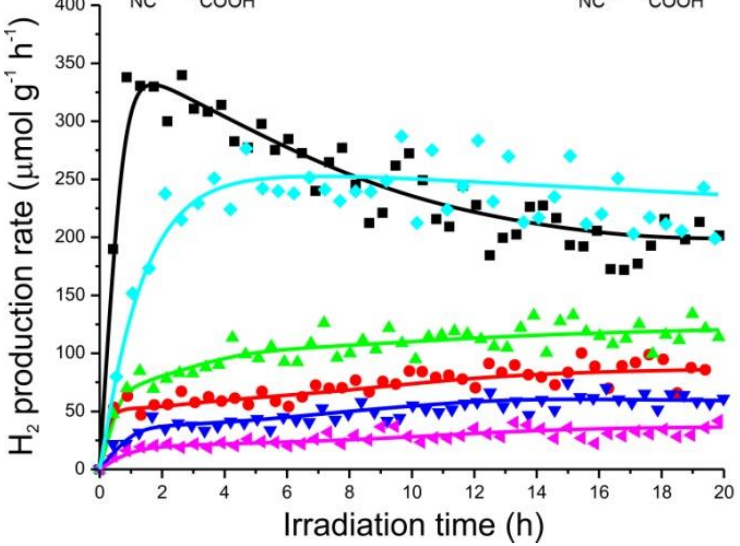
Effect of molecular structure



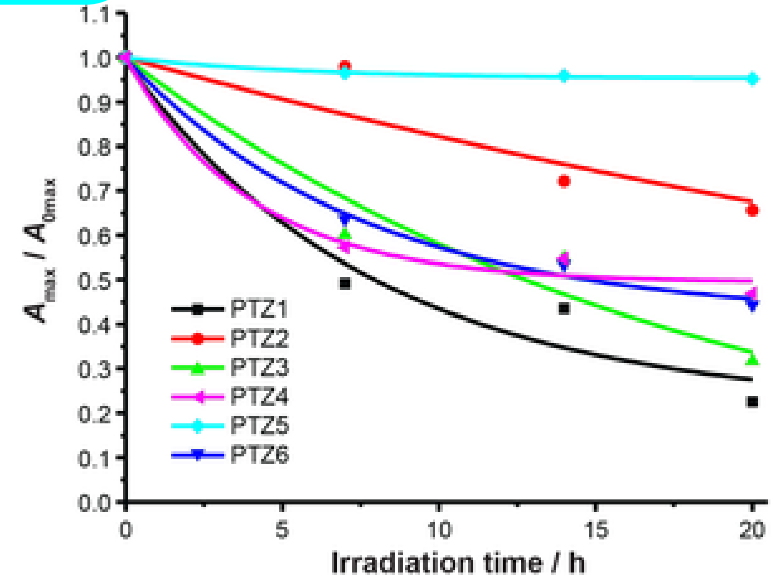
ChemSusChem **8** (2015), 4216-4228

Effect of molecular structure





Active & Stable



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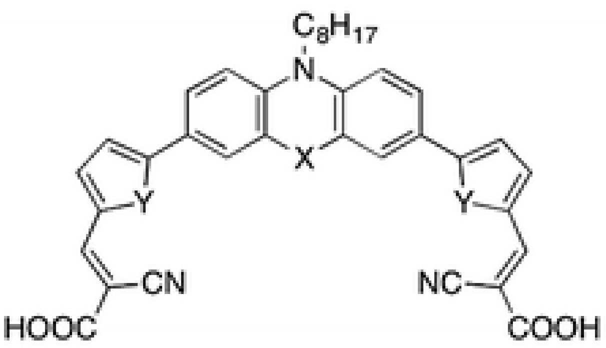
PHENOTIAZINE-BASED DYES

Effect of aromatic structure



PTZ-Th: X = S, Y = S
PTZ-Fu: X = S, Y = O

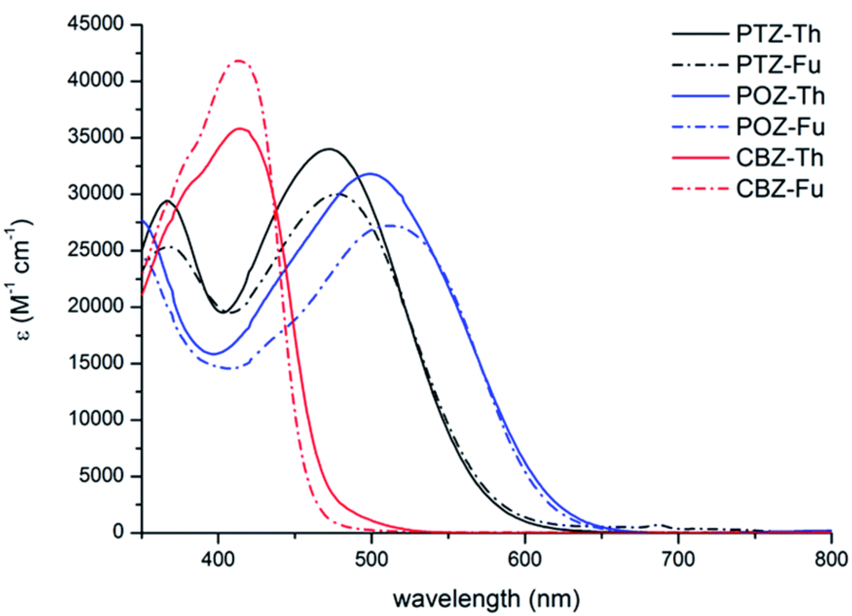
Phenotiazine

POZ-Th: X = O, Y = S
POZ-Fu: X = O, Y = O

Phenoxazine

CBZ-Th: X = none, Y = S
CBZ-Fu: X = none, Y = O

Carbazole



Sustain. Energ. Fuels, **1** (2017), 694-698

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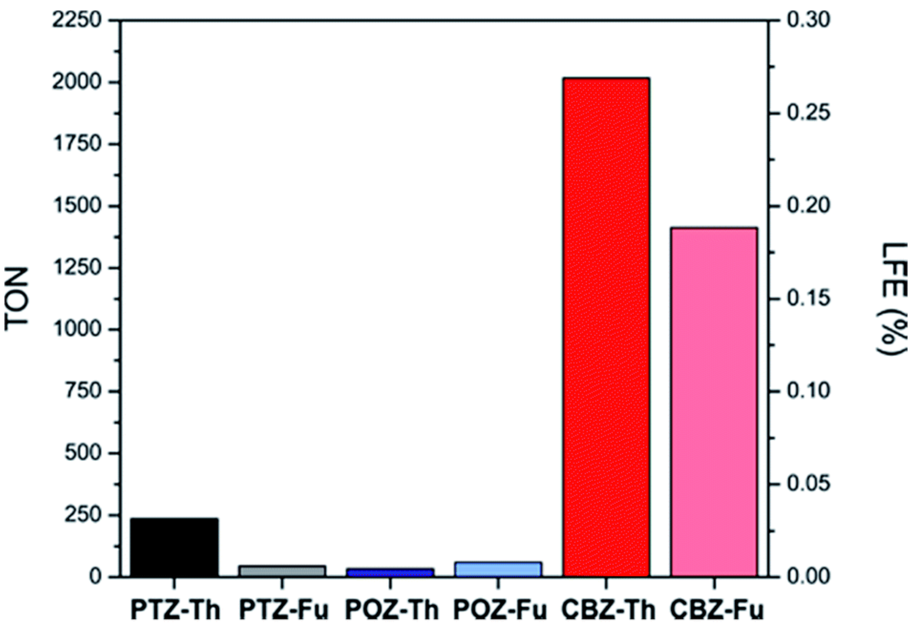
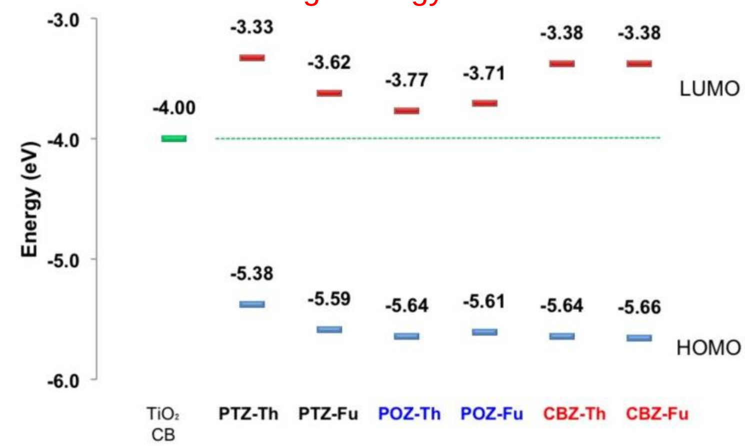
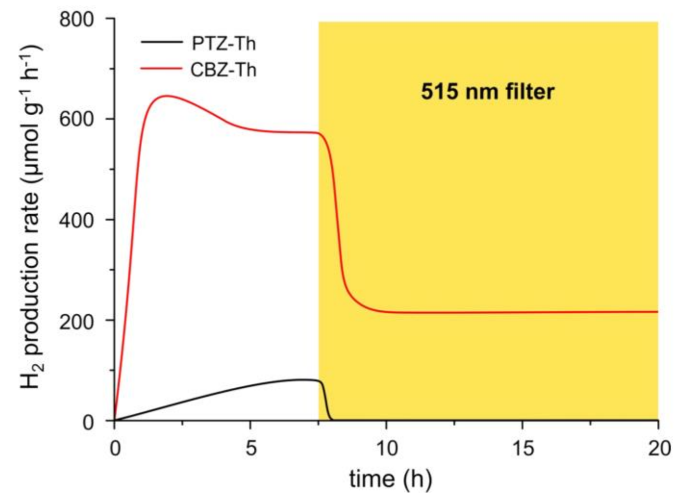


High energy of LUMO



Ligand-to-Metal Charge Trasfer



Sustain. Energ. Fuels, **1** (2017), 694-698

Toward sustainability

EtOH / water solution
as sacrificial electron donor
$\lambda > 420$ nm

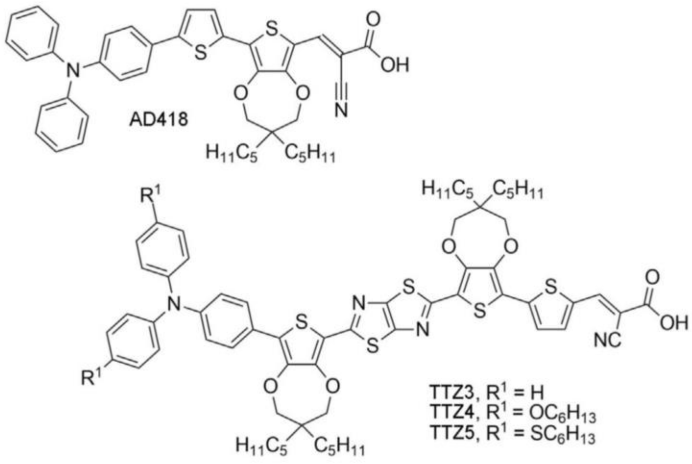
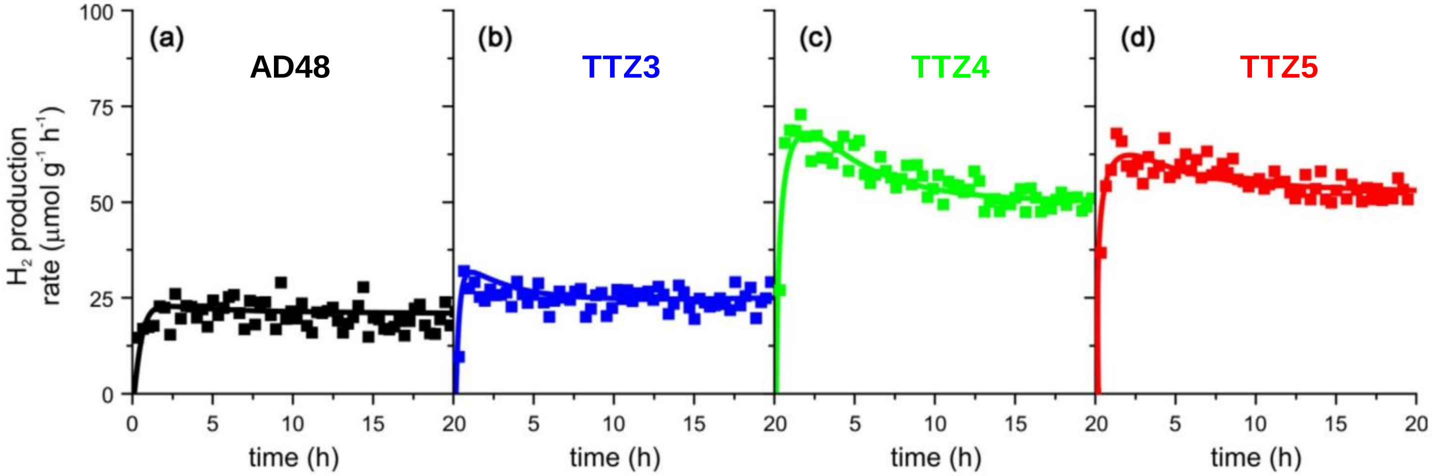


Figure 2. Structure of the dyes investigated in this study.



ChemSusChem 11 (2018), 793-805

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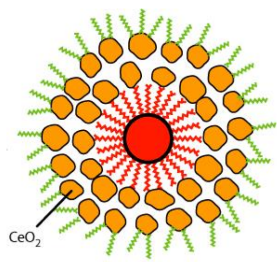

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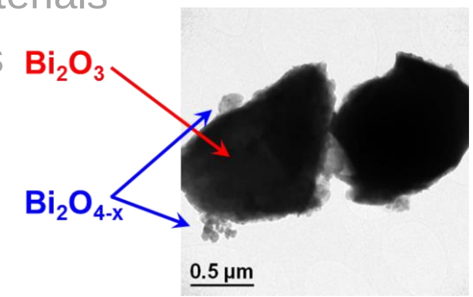

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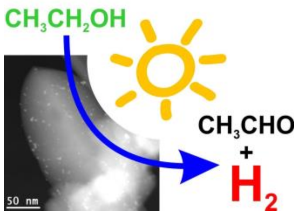

H_2 purification

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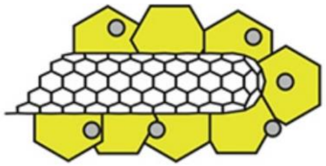


$Pd@CeO_2/MWCNT$

ELECTRICAL VEHICLES

Electric Vehicles Smart Fleets

Electric Unmanned aerial vehicles

ELECTRIC / HYBRID AIRCRAFT

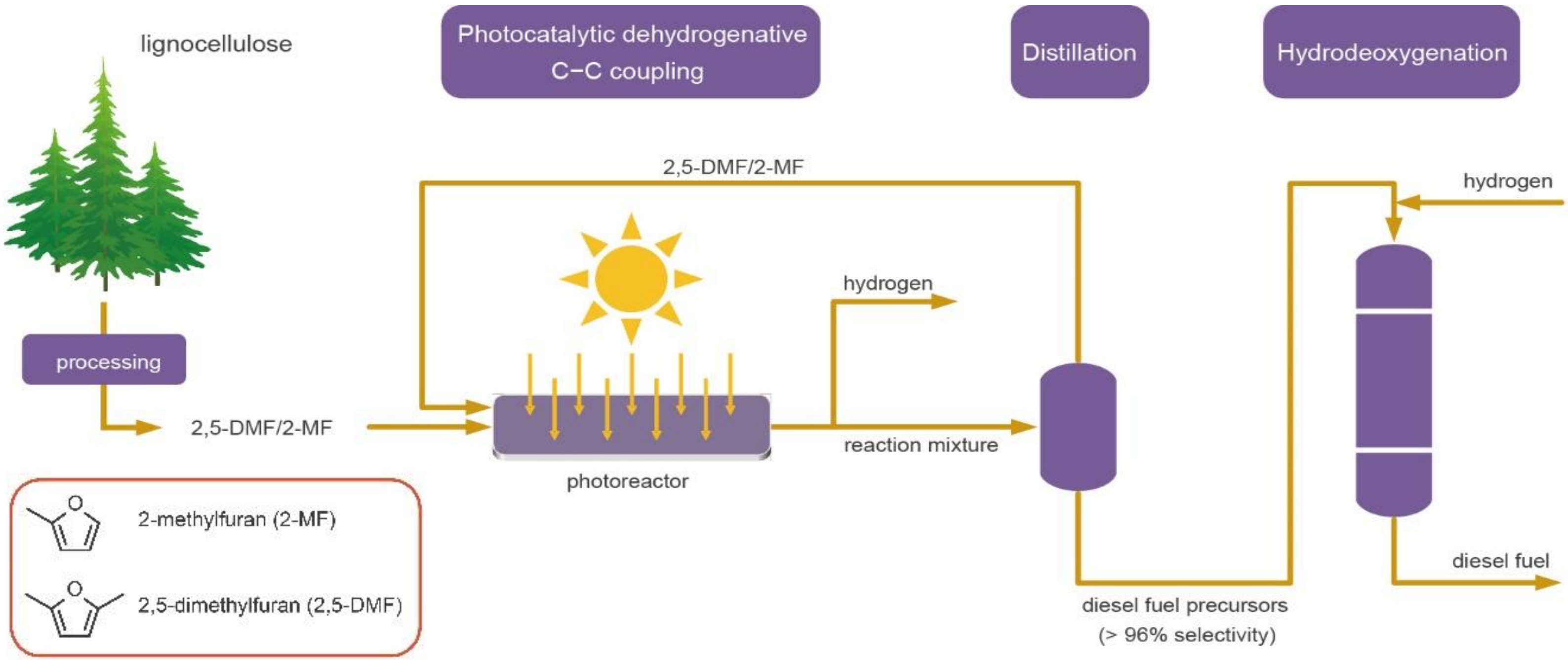
2 hrs 250 Kg of batterie

1 MJ/Kg

43 MJ/Kg

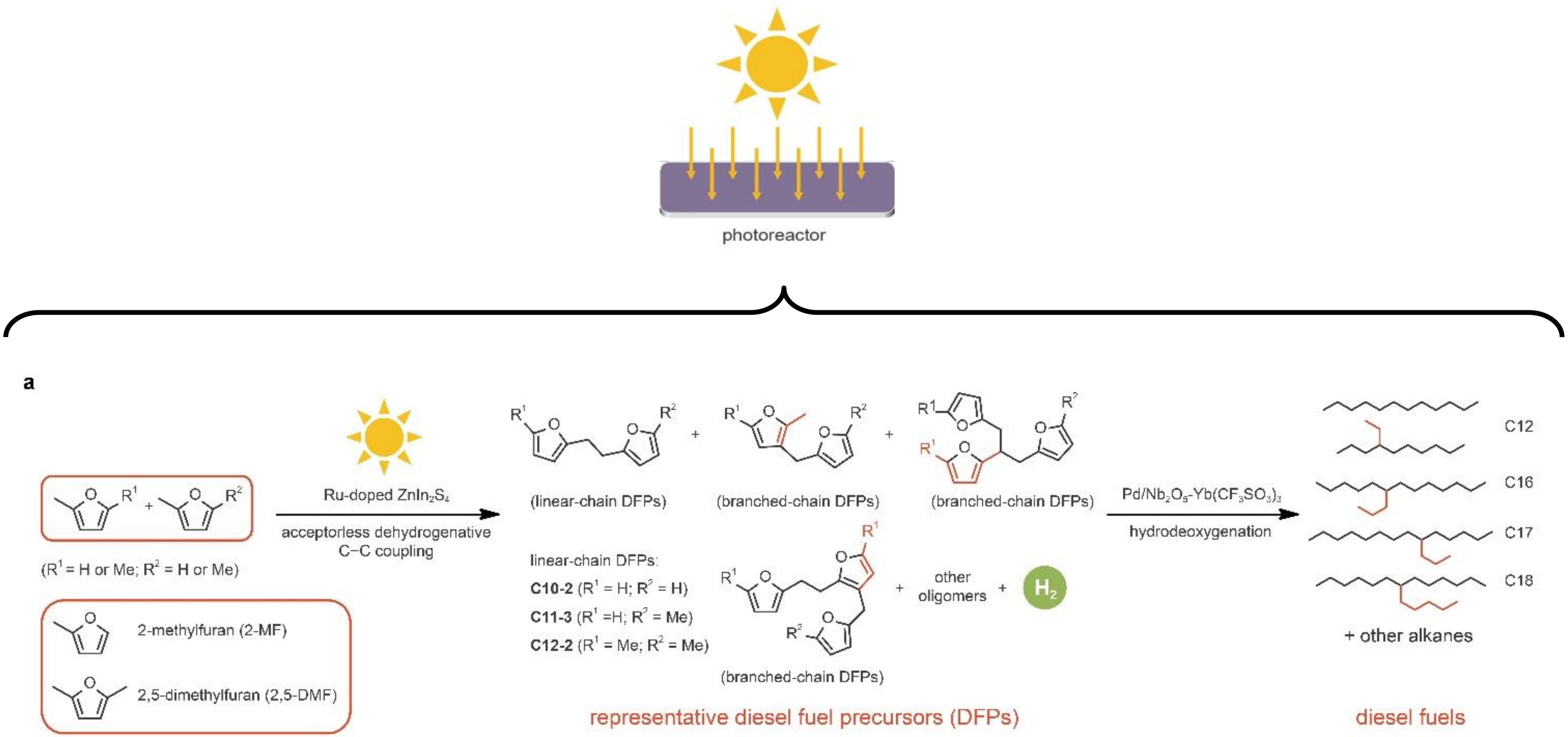
7 hrs 260,000 Kg of batteries

VISIBLE-LIGHT-DRIVEN COPRODUCTION OF DIESEL FUEL PRECURSORS AND HYDROGEN



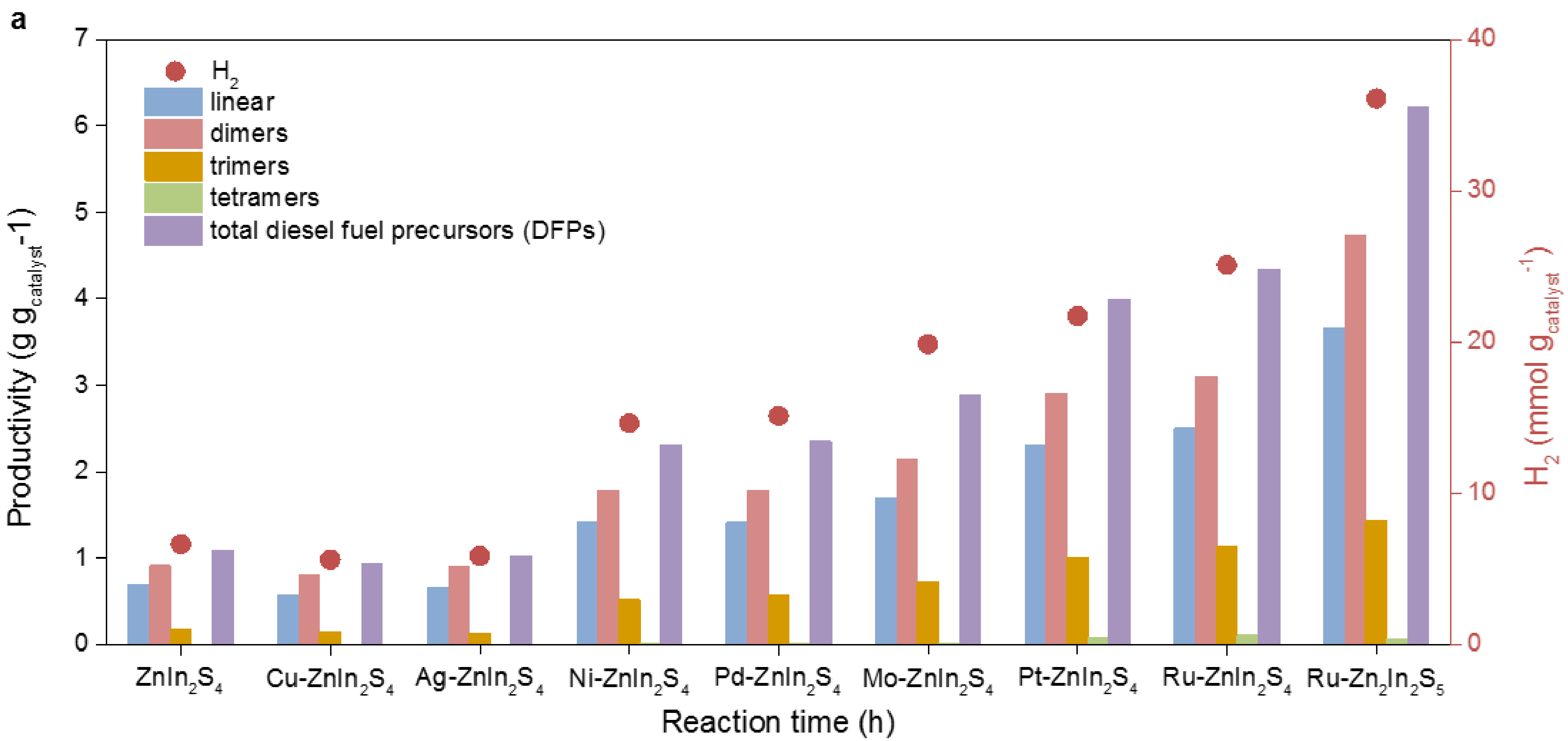
Nature Energy **4** (2019), 575-584

VISIBLE-LIGHT-DRIVEN COPRODUCTION OF DIESEL FUEL PRECURSORS AND HYDROGEN



Nature Energy **4** (2019), 575-584

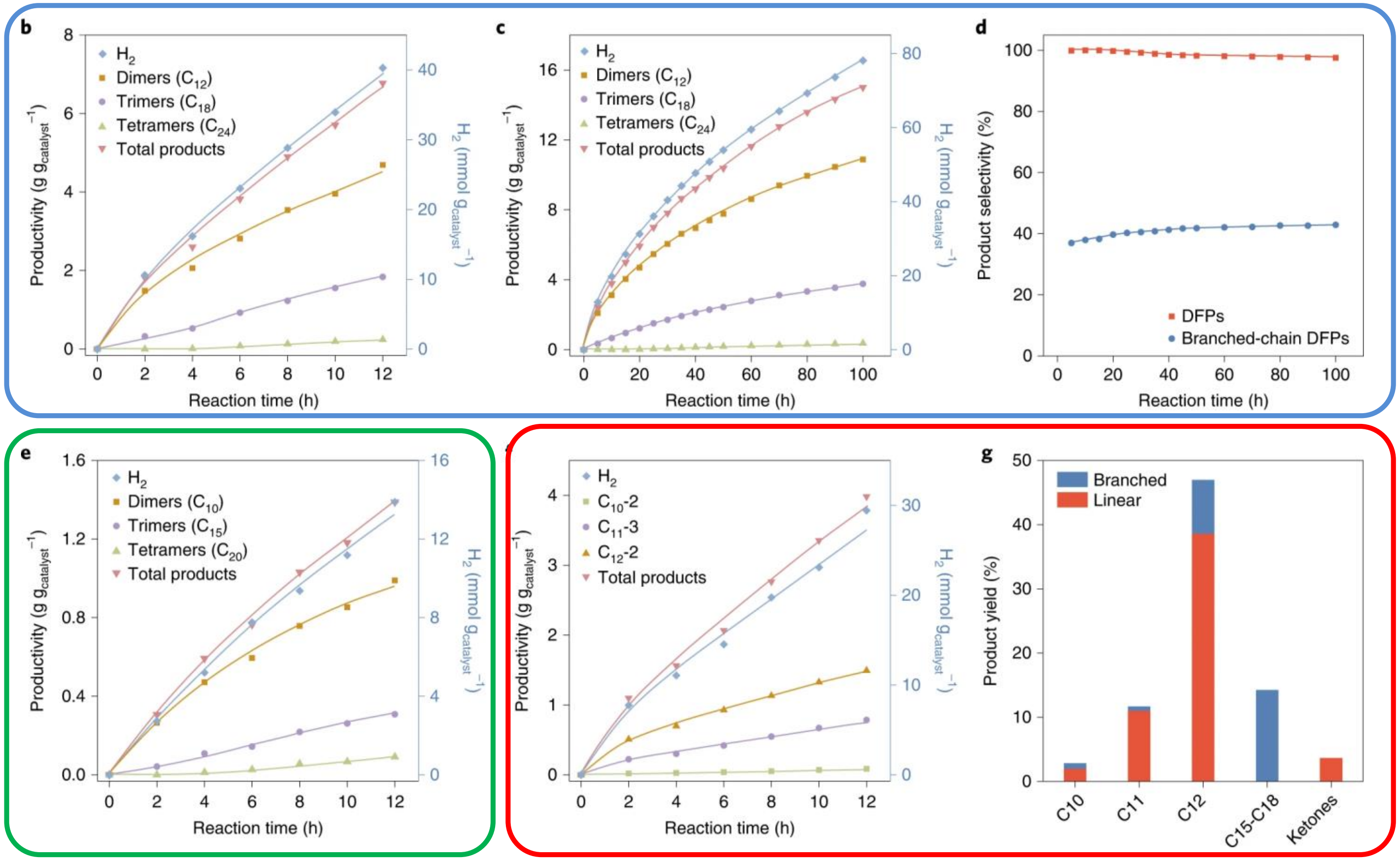
Doped-$ZnIn_2S_4$ photocatalysts



Nature Energy **4** (2019), 575-584

VISIBLE-LIGHT-DRIVEN COPRODUCTION OF DIESEL FUEL PRECURSORS AND HYDROGEN

Ru-$ZnIn_2S_4$ photocatalyst



2,5-DMF

0.56 g of DPF g_{cat}^{-1} h^{-1}

3.3 mmol of H_2 g_{cat}^{-1} h^{-1}

AQY 15.2 %

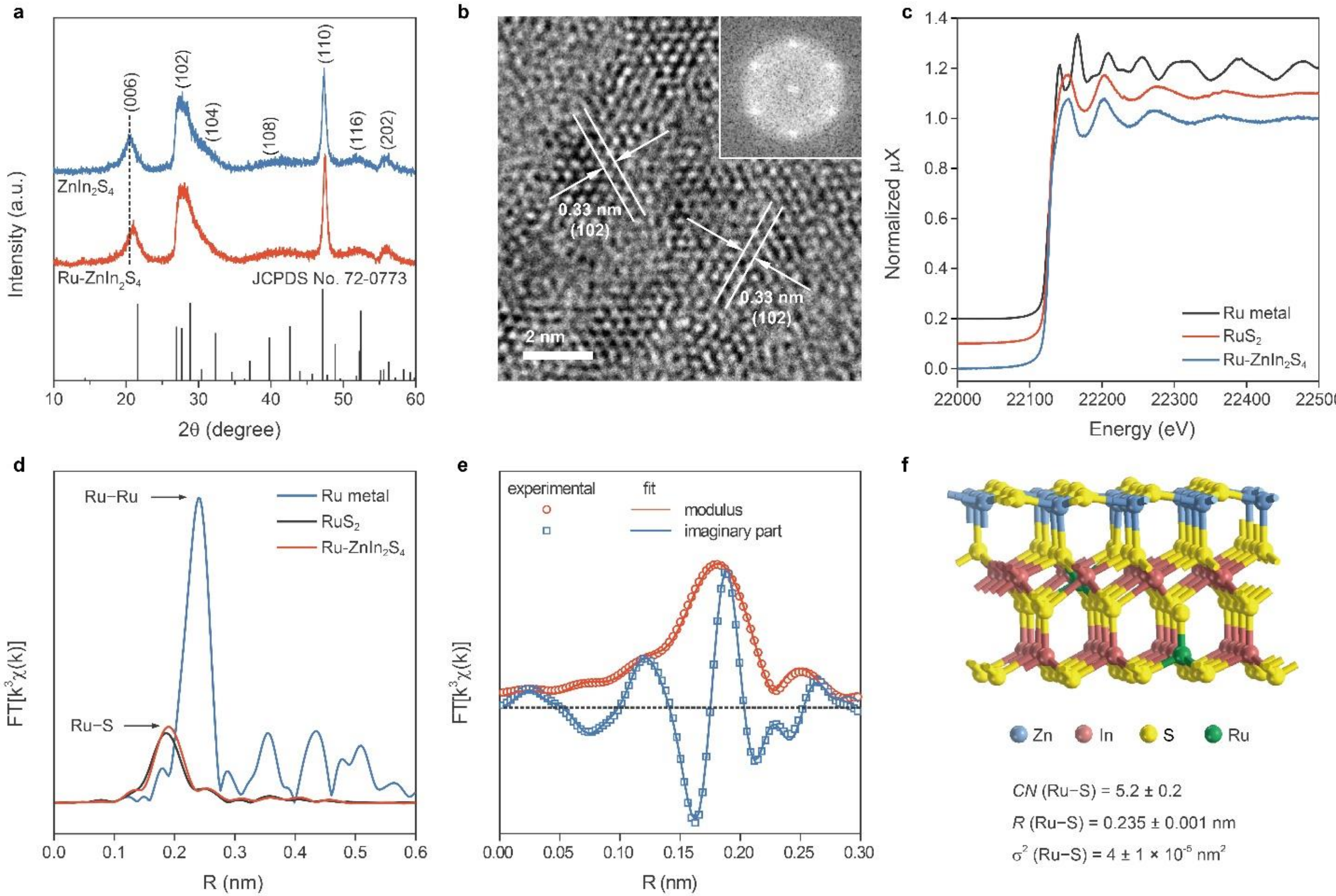
2-MF

2,5-DMF + 2-MF

Nature Energy **4** (2019), 575-584

VISIBLE-LIGHT-DRIVEN COPRODUCTION OF DIESEL FUEL PRECURSORS AND HYDROGEN

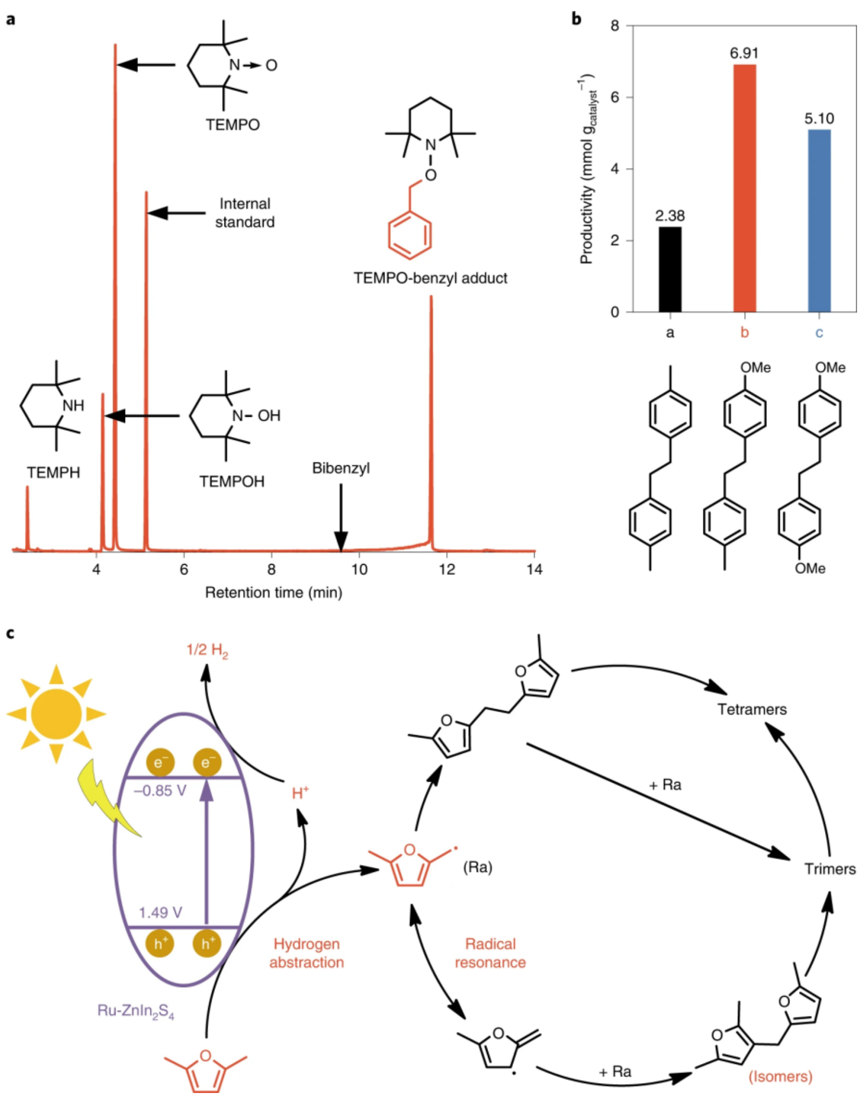
Ru-$ZnIn_2S_4$ photocatalyst



Nature Energy **4** (2019), 575-584

VISIBLE-LIGHT-DRIVEN COPRODUCTION OF DIESEL FUEL PRECURSORS AND HYDROGEN

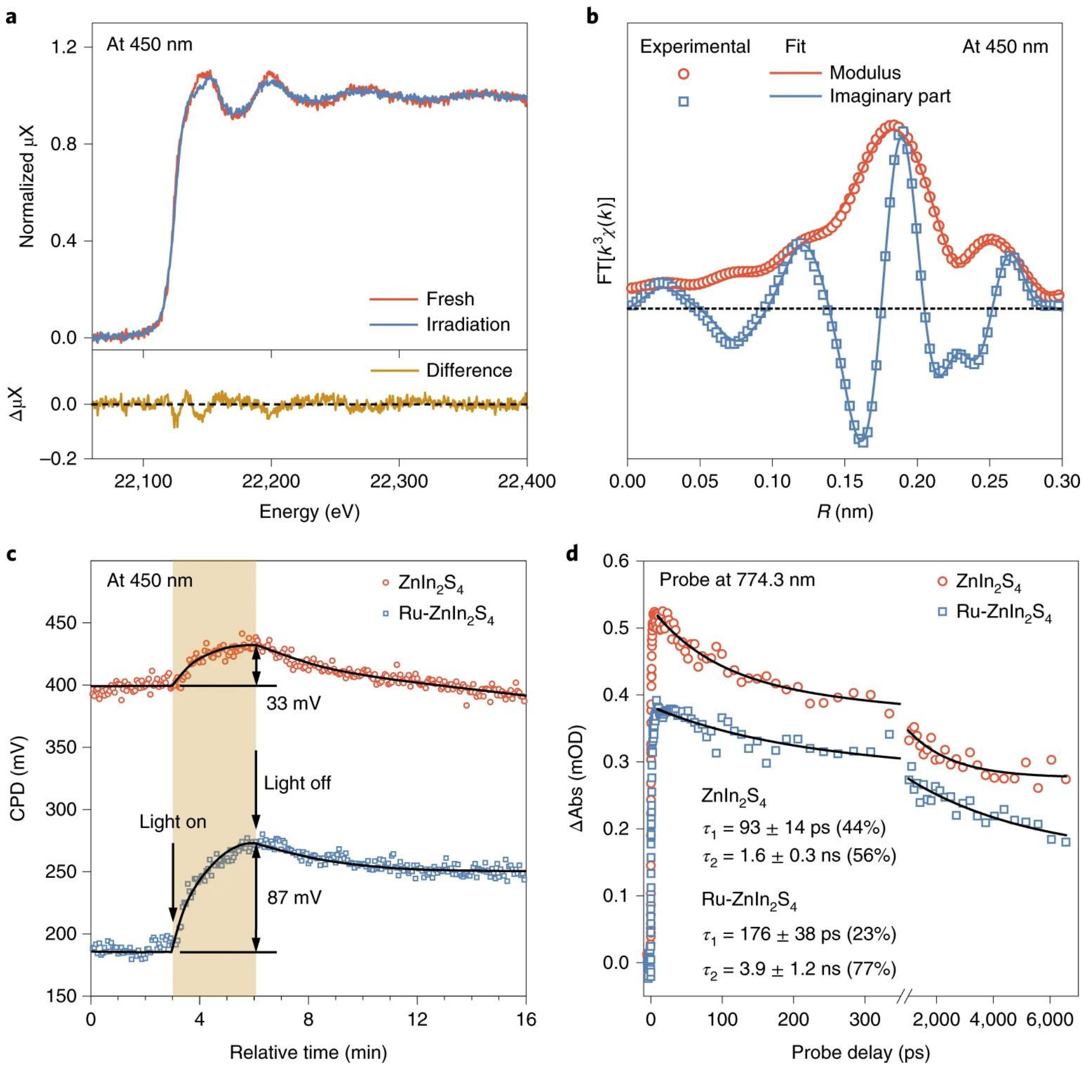
Ru-$ZnIn_2S_4$ photocatalyst



Radical mechanism confirmed

Nature Energy **4** (2019), 575-584

Ru-$ZnIn_2S_4$ photocatalyst: role of Ru



- ✓Decreased band gap
- ✓Stabilization of e^-/h^+ pairs
- ✓Reduction of Ru ions to Ru(0) justifies slight deactivation

Nature Energy **4** (2019), 575-584

PERSPECTIVES

Materials manipulation at nanoscale level and
precise assembly of nano-building blocks
in hierarchical materials can lead to
a step change in photo-, electro- & catalytic performances.

We have great options for a sustainable world!

The future is bright but there are still lots of shadows.

ACKNOWLEDGEMENTS

Group members:
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Dr. Valentina Gombac, Dr. Manuela Bevilacqua
Dr. F. Longobardo, Dr. T.H. Dolla,
Dr. M. Ferrara, Dr. M. Daka

Collaborators:
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Dr. E. Fonda (Soleil - France)
Prof. J.J. Delgado (Univ Cadiz - Spain)
Dr. N. Manfredi, Prof. A. Abbotto (Univ. Milano Bicocca - Italy)

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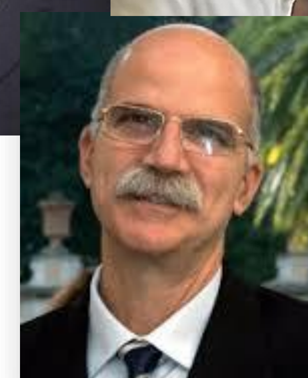
Chinese Academy of Sciences
University of Trieste, FRA 2018 Projects
INSTM & ICCOM-CNR

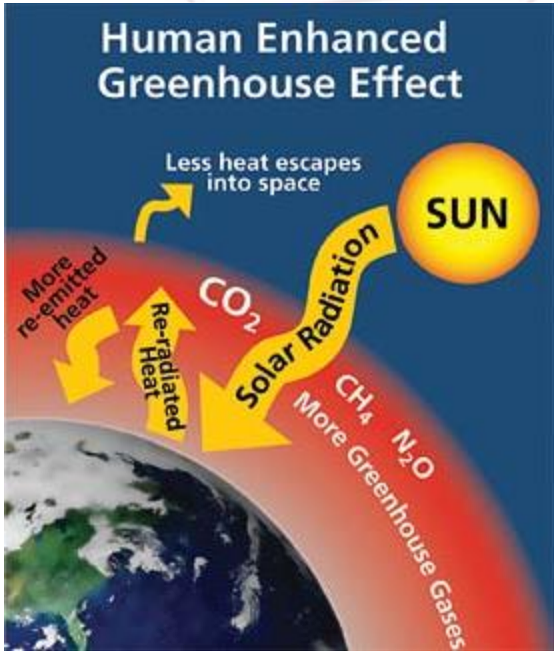


http://meeresearch.weebly.com/

THANK YOU ALL FOR YOUR KIND ATTENTION

MINING REQUIRES ENERGY

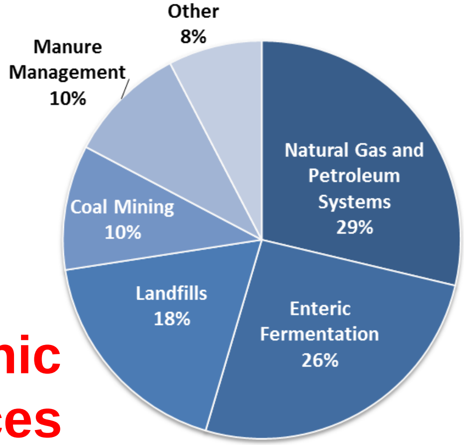
CH_4 & GREENHOUSE EFFECT



- Lifetime in the atmosphere is much shorter than CO_2
- More efficient at trapping radiation than CO_2

Impact of CH_4 on climate change is more than 25 times greater than CO_2

Source Identification and Quantification



Anthropogenic sources

EPA, Emission Overview 2015

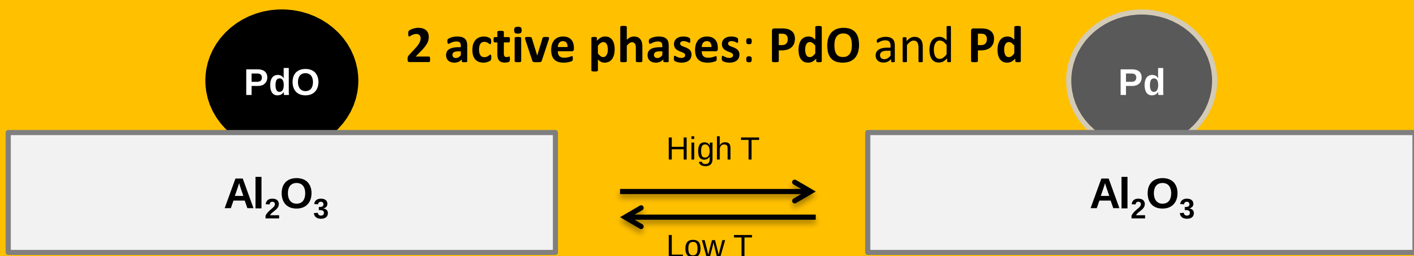
NEEDS FOR CATALYTIC ABATEMENT

Pd-BASED CH_4 COMBUSTION CATALYSTS

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

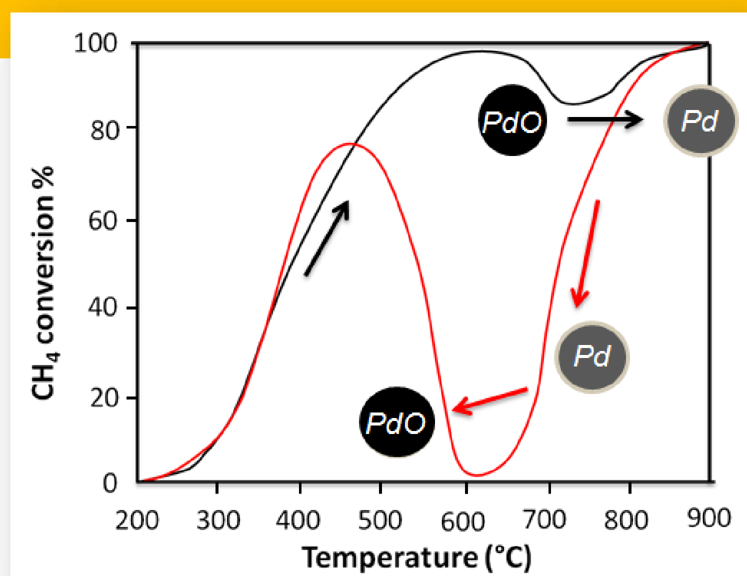
Noble metal-based catalysts (Pd, Pt, Au)

2 active phases: PdO and **Pd**



High specific activity

Lower specific activity

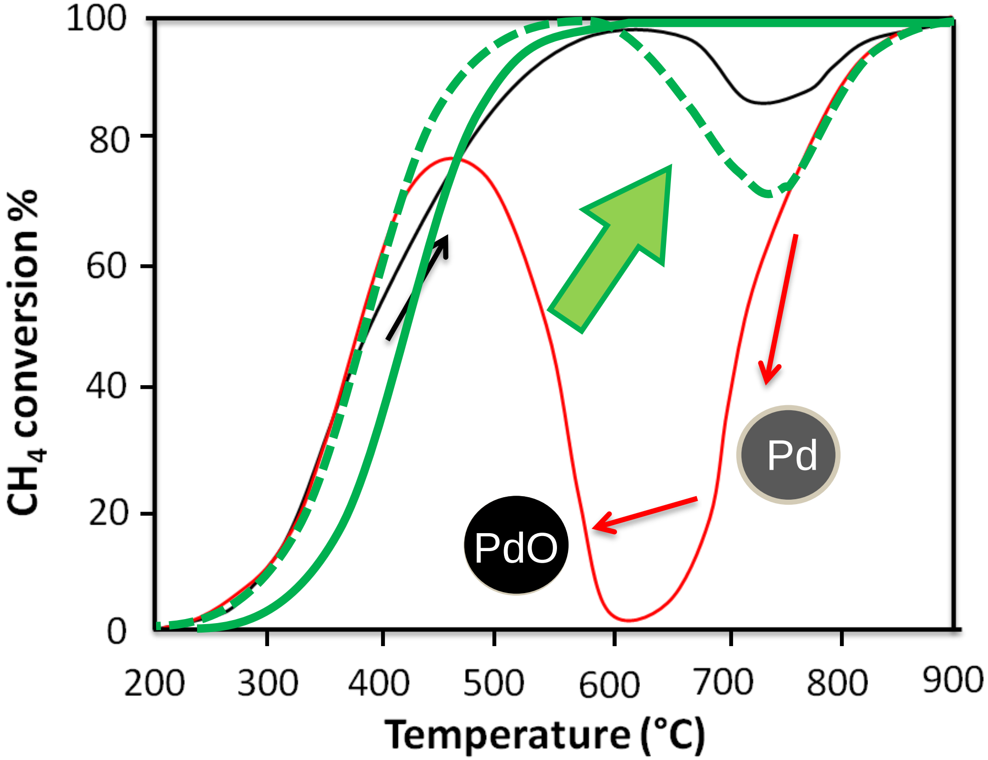


Pd(5%)/La-Al_2O_3

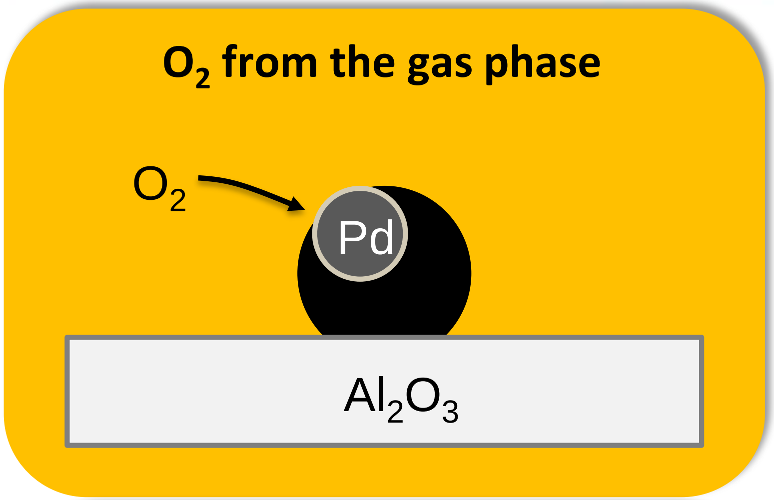
P. Gélin, M. Primet, *Appl. Catal. B-Environ.* **39** (2002**)**, 1-37

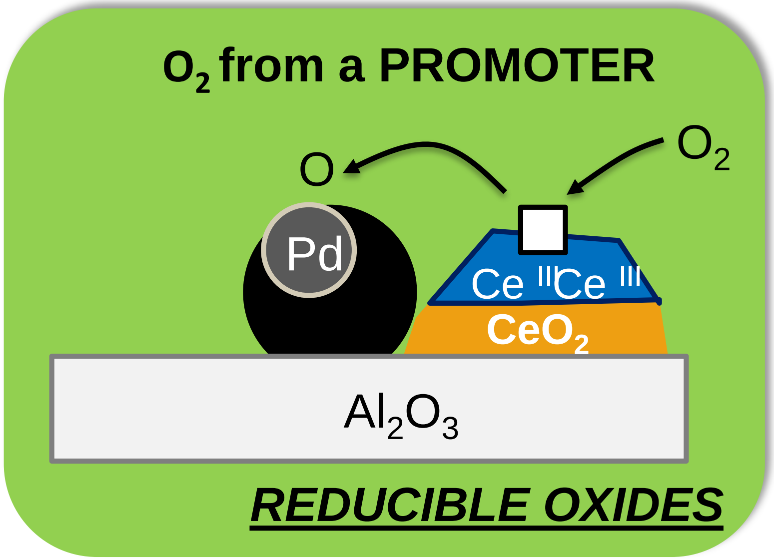
Pd-BASED CH_4 COMBUSTION CATALYSTS

Catalyze re-oxidation

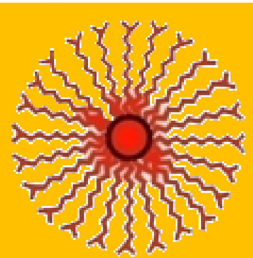


Maximize PdO - CeO_2 interaction





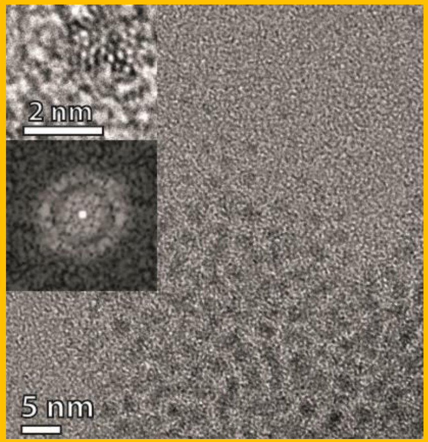
Pd@CeO_2 SUPRAMOLECULAR STRUCTURES



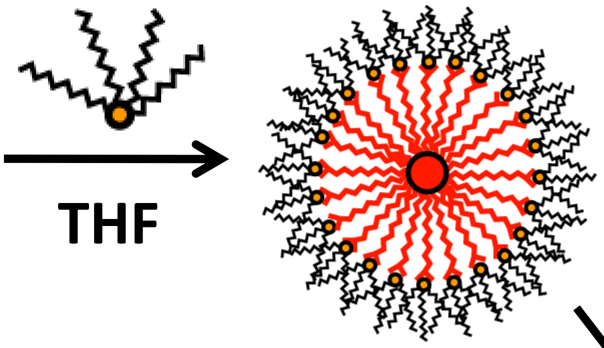
MUA-Pd NPs

MUA: 11-Mercapto Undecanoic Acid

Pd core size: 1.8 ± 0.2 nm

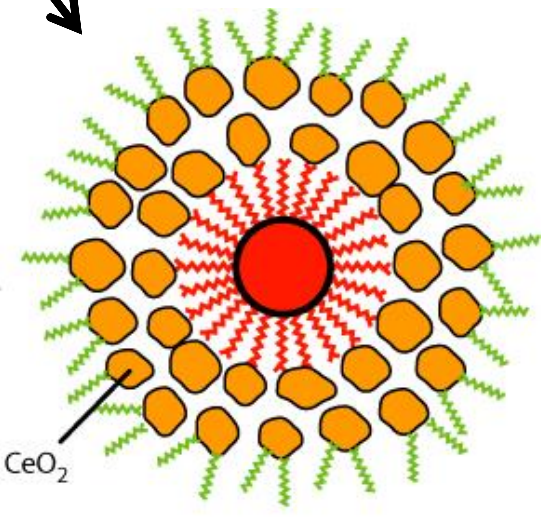


Ce(IV) tetrakis(decyloxide)



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

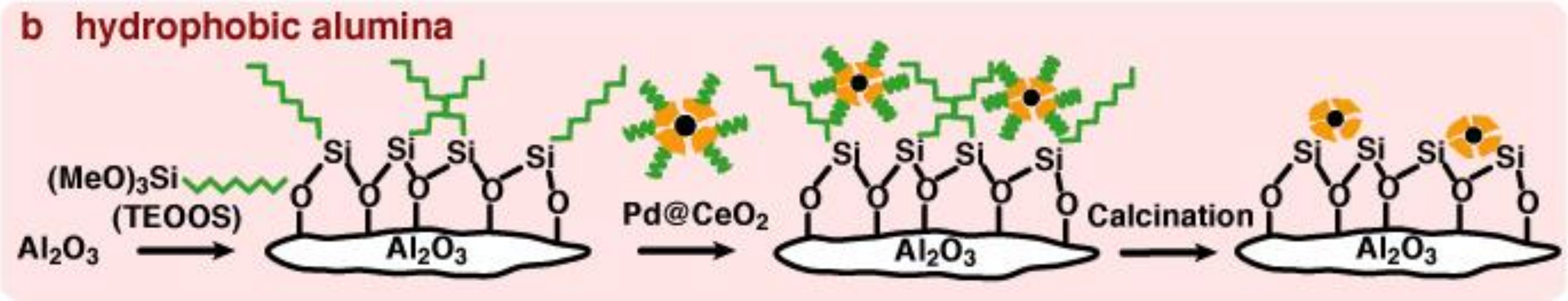
Dodecanoic Acid (DA) +
Controlled Hydrolysis



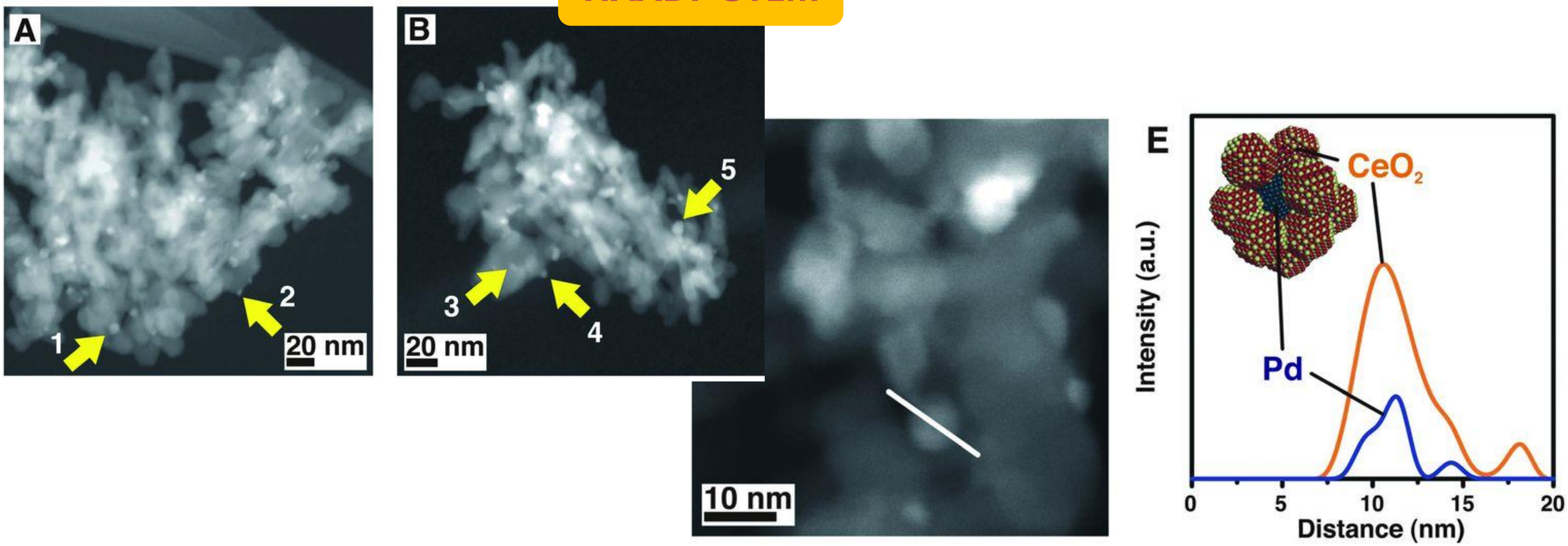
Dispersible in CH_2Cl_2, toluene, hexane

J. Am. Chem. Soc. **132** (2010), 1402-1409

Pd@CeO_2 FOR CH_4 COMBUSTION

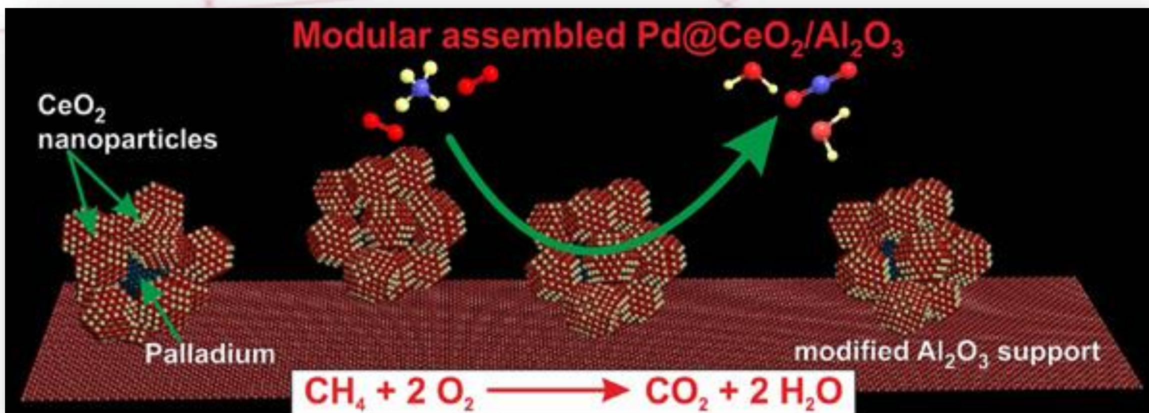


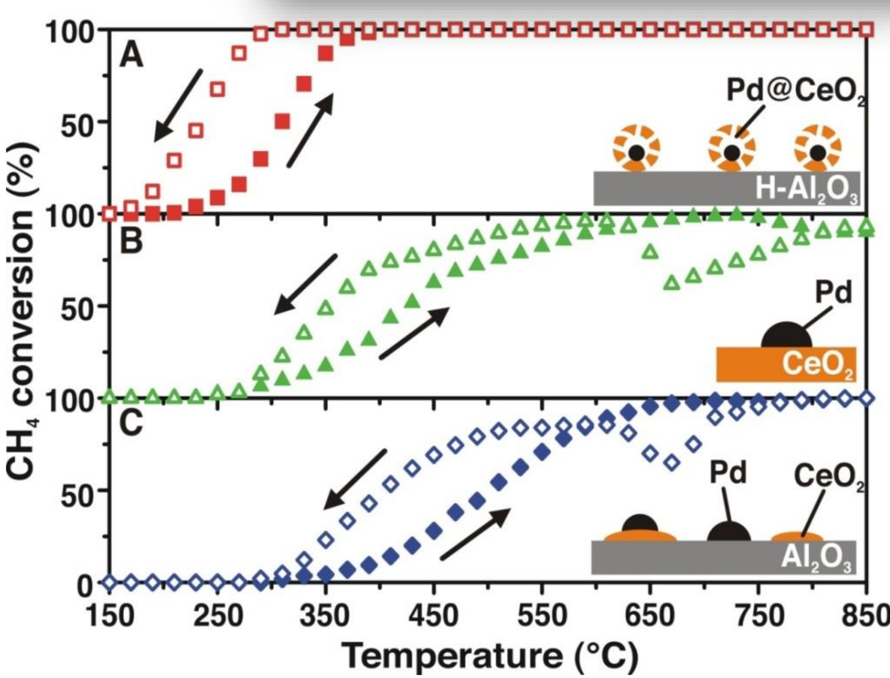
HAADF-STEM

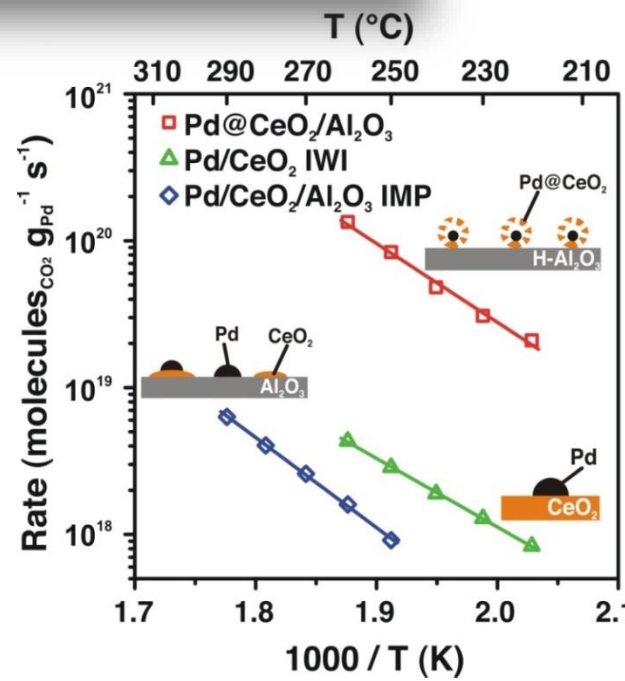


Science **337** (2012), 713-717

Pd@CeO_2 FOR CH_4 COMBUSTION

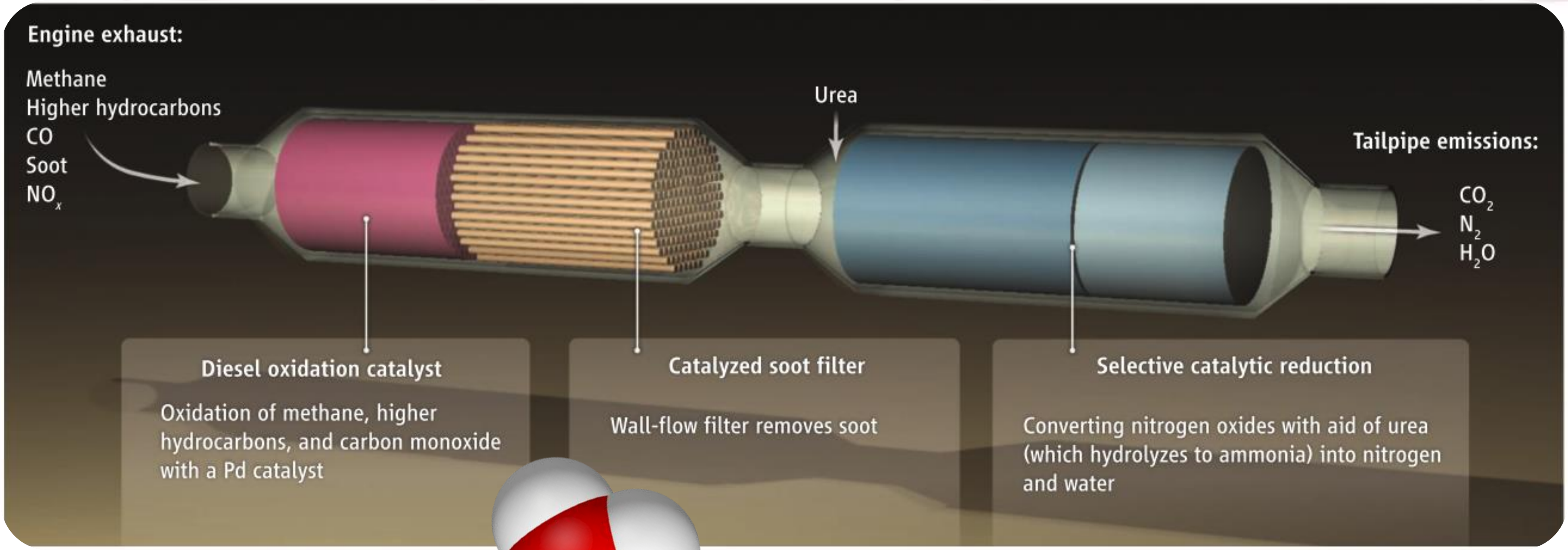


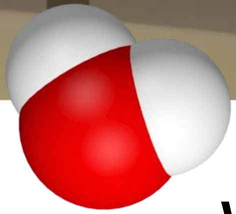




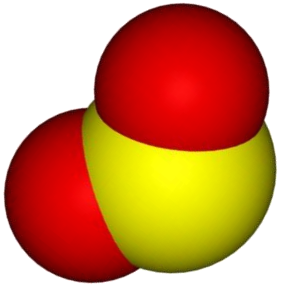
Science **337** (2012), 713-717

Pd@CeO$_2$ FOR CH$_4$ COMBUSTION

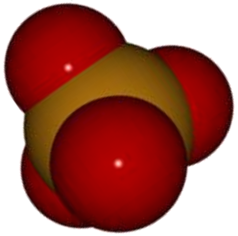




Water vapor



SO$_2$



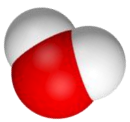
Phosphates

PdO DEACTIVATION

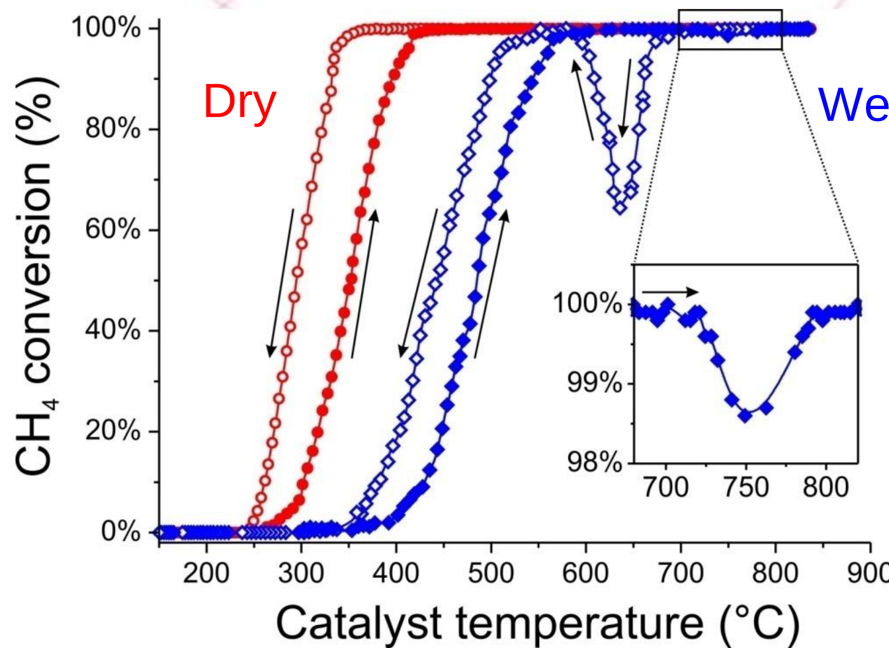
R. Farrauto, *Science* **337** (2012), 659

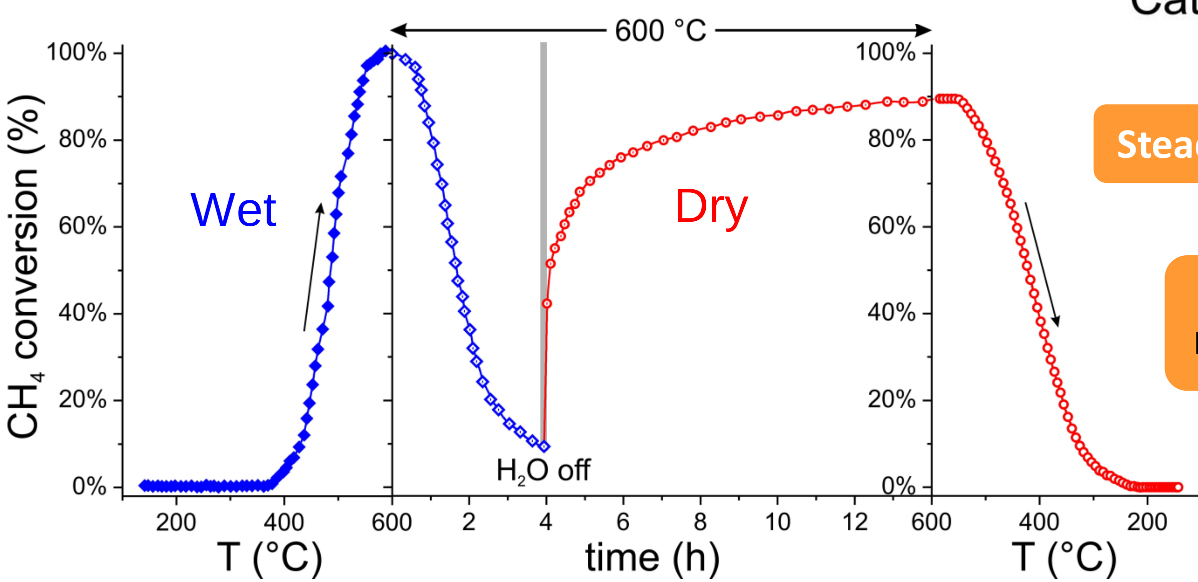
Pd@CeO_2 FOR CH_4 COMBUSTION

Light Off



Effect of water





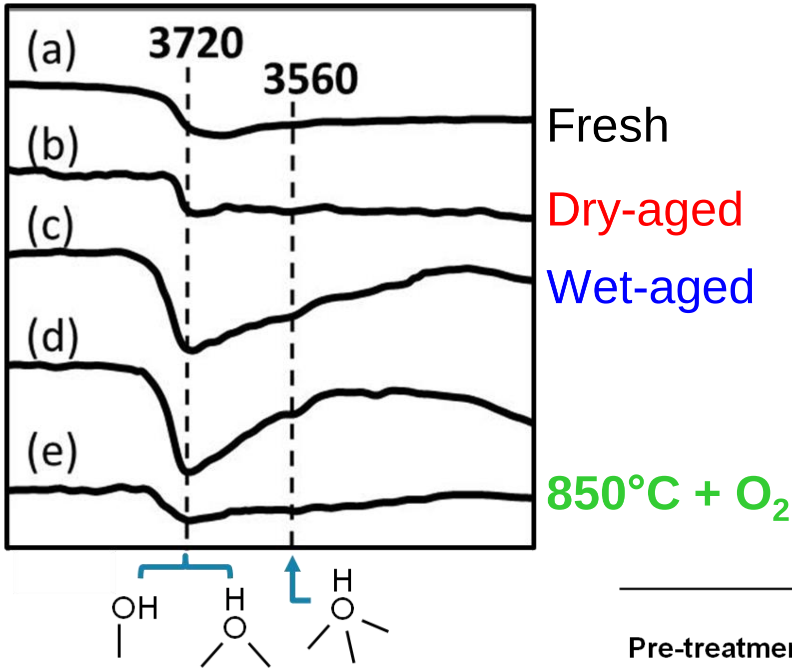
Steady State

0.5% CH_4, 2.0% O_2, 15% H_2O (if present), Ar balance, $O_2/O_{2(stoich)}$=2, GHSV = 200000 mL g^{-1} h^{-1}

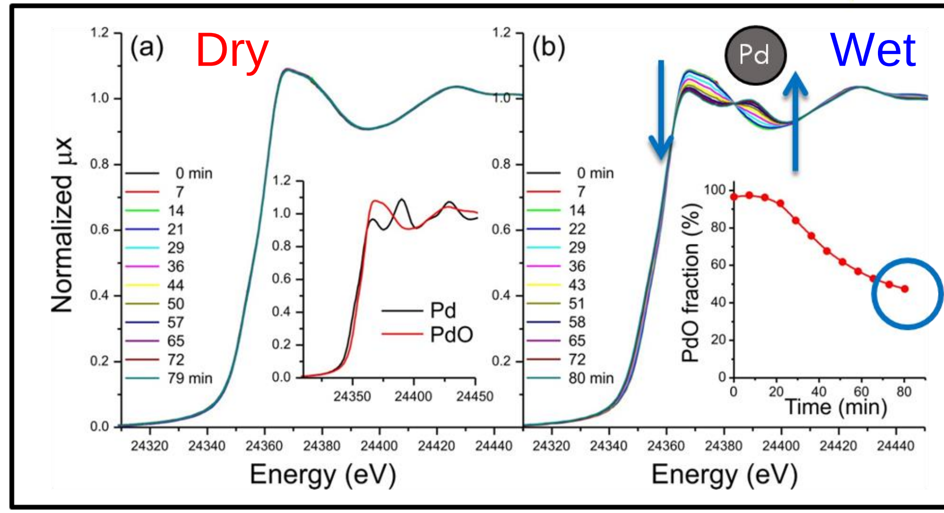
ChemCatChem **7** (2015), 2038-2046

Pd@CeO_2 FOR CH_4 COMBUSTION

IR



EXAFS

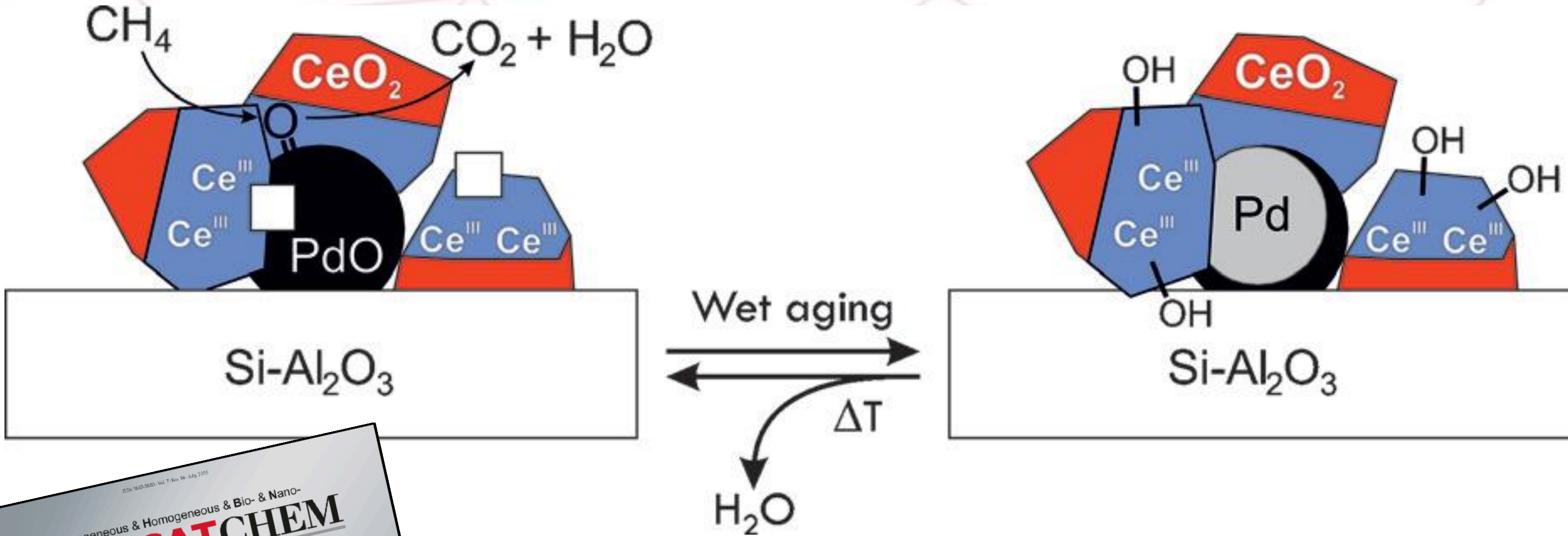


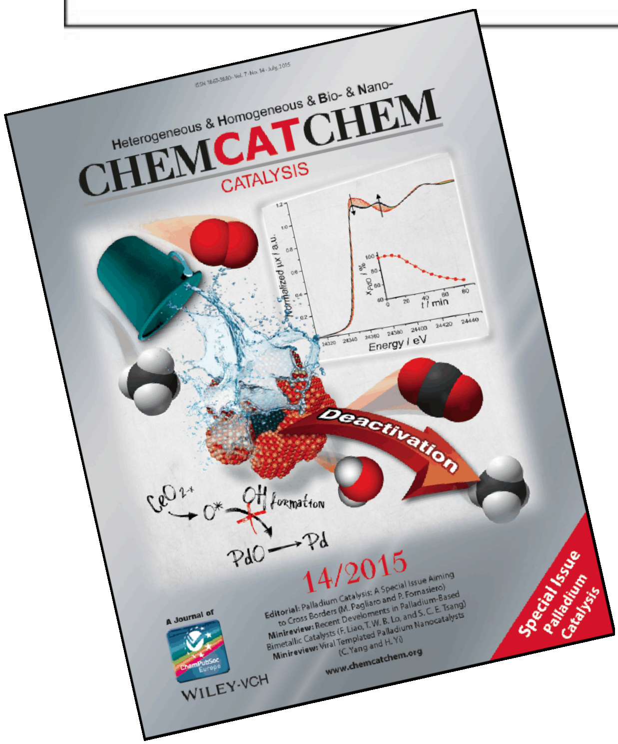
Chemisorption

Pre-treatment	Accessible Pd surface area (m^2/g)
Fresh	3.0
Dry aged	2.8
Reactivated after dry aging	3.3
Wet aged	1.1
Reactivated after wet aging	3.2

ChemCatChem **7** (2015), 2038-2046

Pd@CeO$_2$ FOR CH$_4$ COMBUSTION





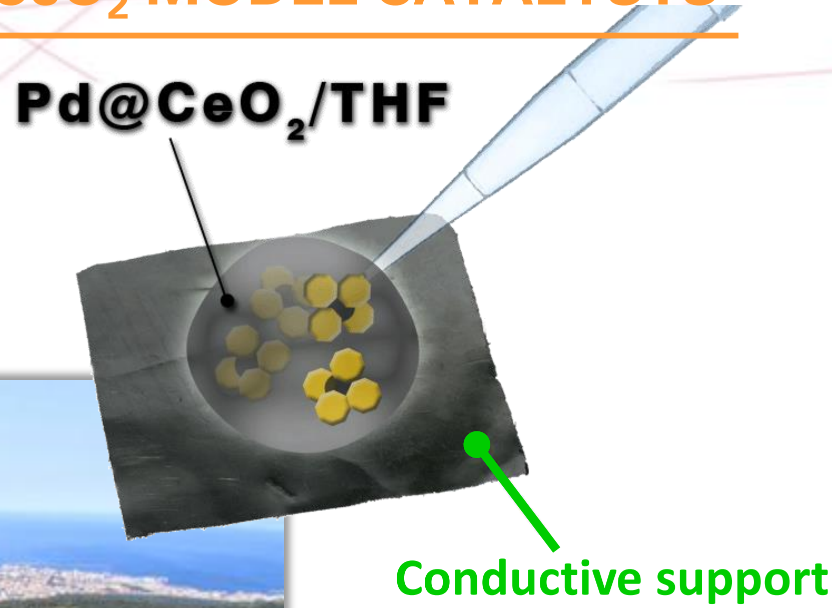
- Reduction of PdO to Pd
- Increase in population of OH
- Wet aging reduces Pd accessibility

ChemCatChem **7** (2015), 2038-2046

$Pd@CeO_2$ MODEL CATALYSTS

XPS-SRPES

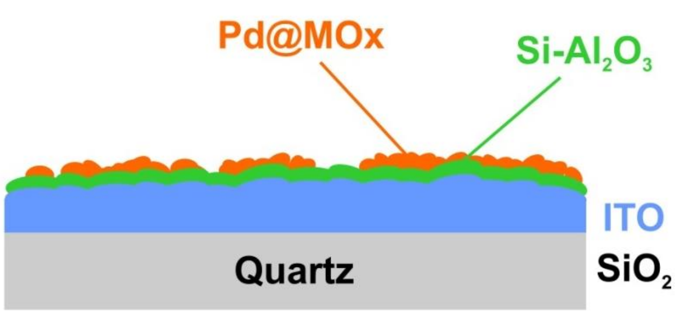
Synchrotron Radiation PhotoEmission Spectroscopy

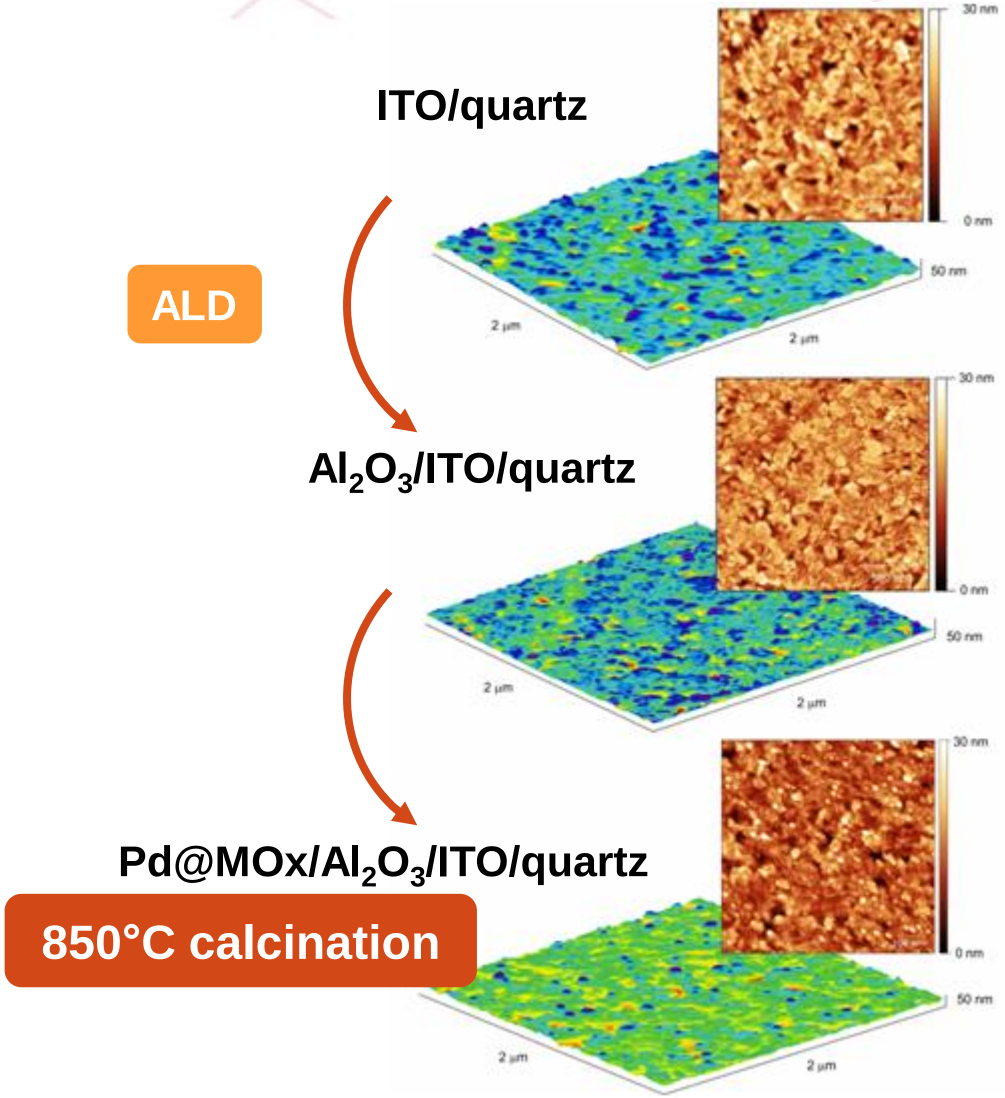


Surface Study

Elettra Sincrotrone Trieste

SURFACE STUDY: SO_2 POISONING



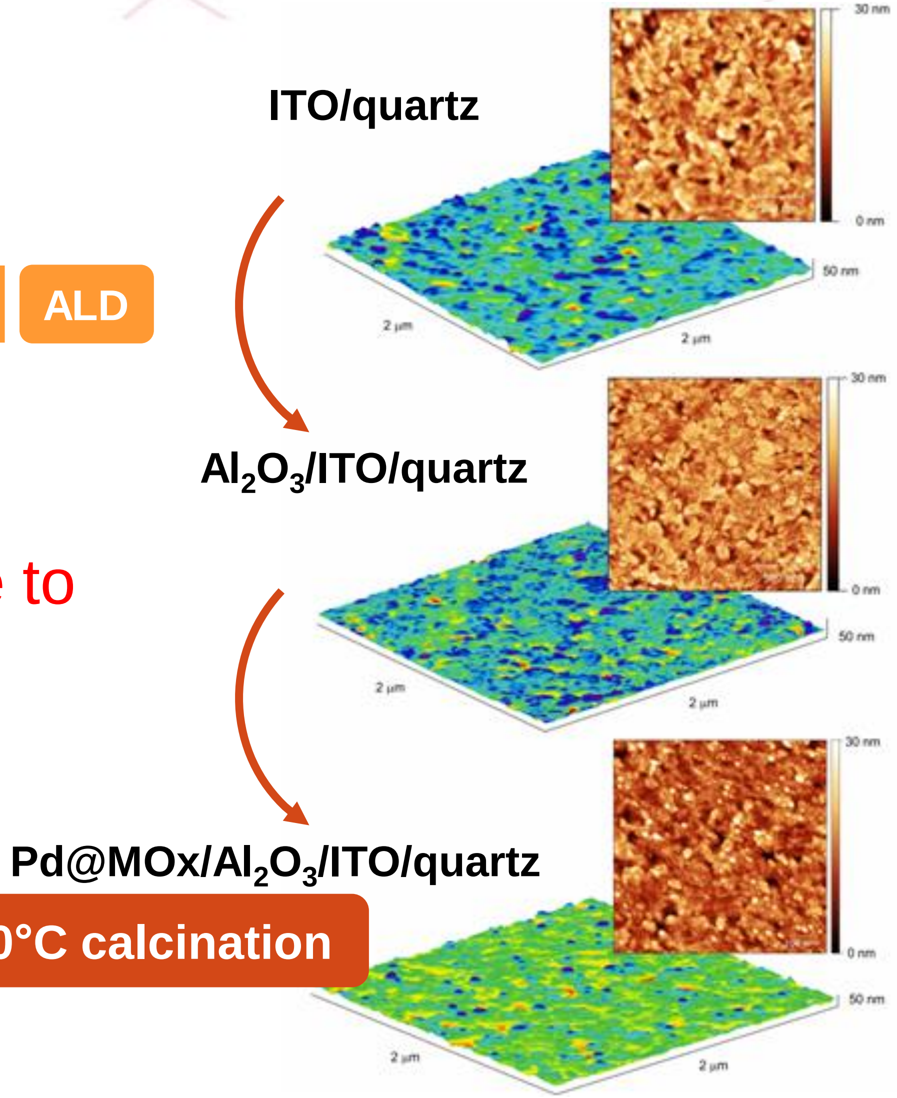


Appl. Catal. B-Environ. **202** (2017), 72-83

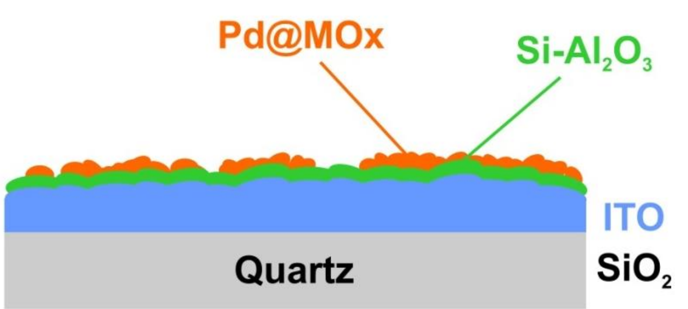
SURFACE STUDY: SO_2 POISONING

- Choose layer composition
- Change thickness
- General applicability

ALD



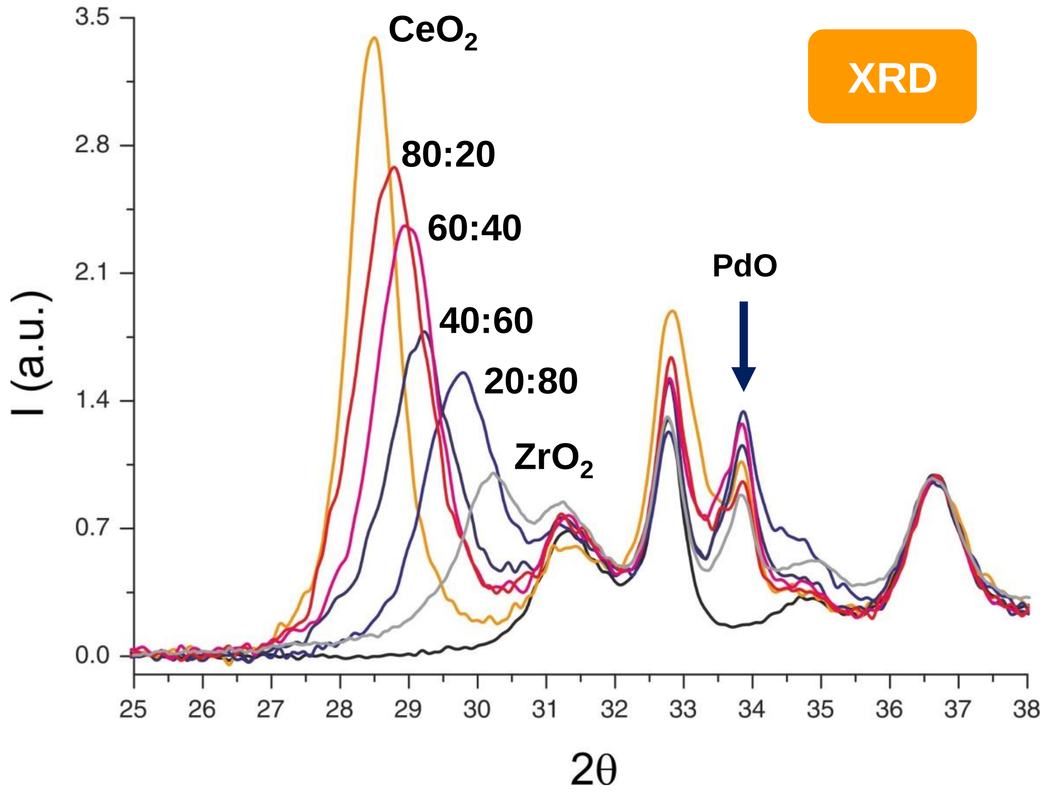
Model materials comparable to real catalysts

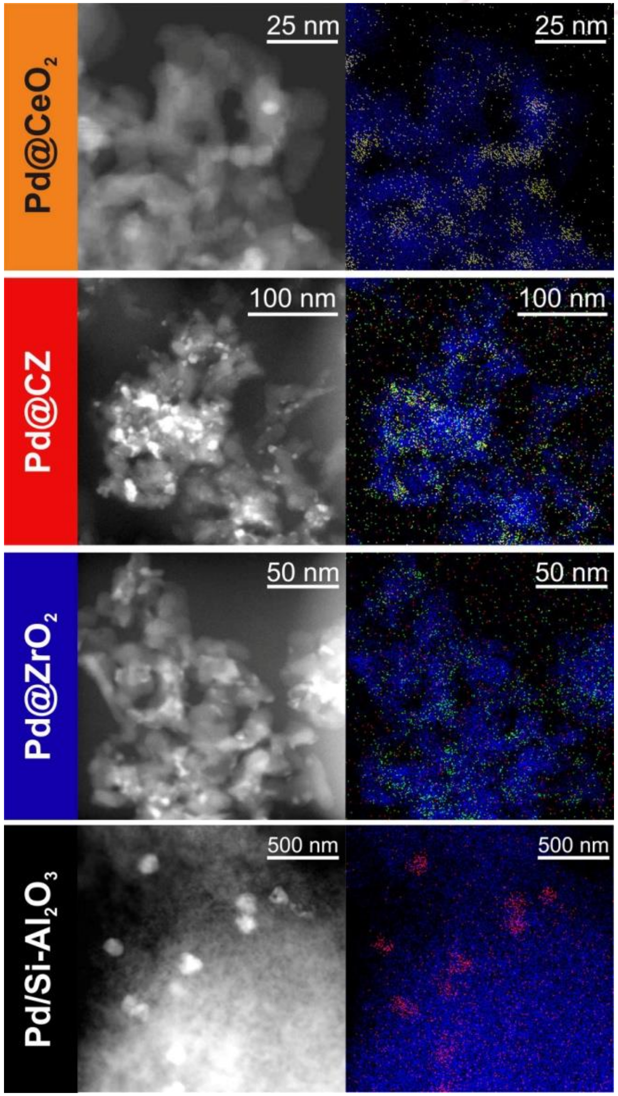


Appl. Catal. B-Environ. **202** (2017), 72-83

SURFACE STUDY: SO_2 POISONING

- **Surface area** 90-100 m^2g^{-1}
- **Pd accessible area** 3 $m^2\,g^{-1}$ (~ 60% D)
- **Similar activity in light off experiments**

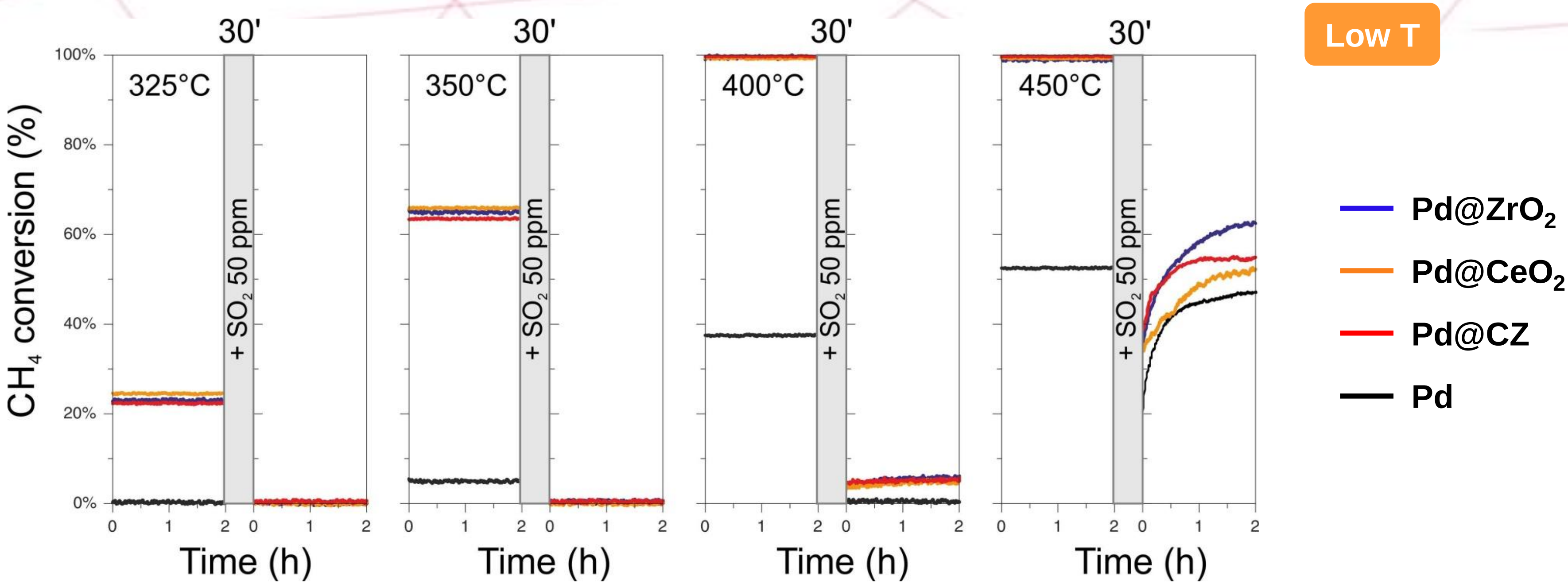




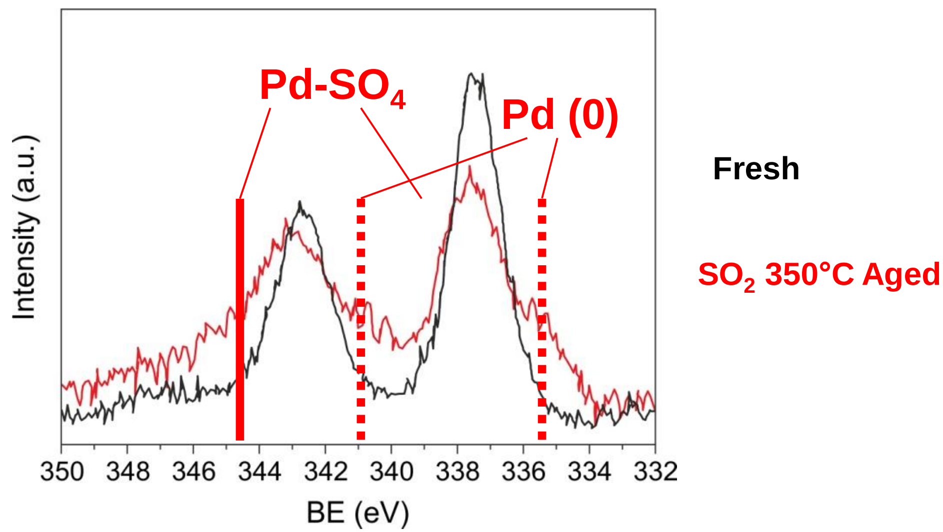
Appl. Catal. B-Environ. **202** (2017), 72-83

SURFACE STUDY: SO_2 POISONING

Low T



0.5% CH_4, 2.0% O_2, SO_2 50 ppm (if present), Ar balance, $O_2/O_{2(stoich)}$=2, GHSV = 200000 mL g^{-1} h^{-1}



Similar performances complete deactivation

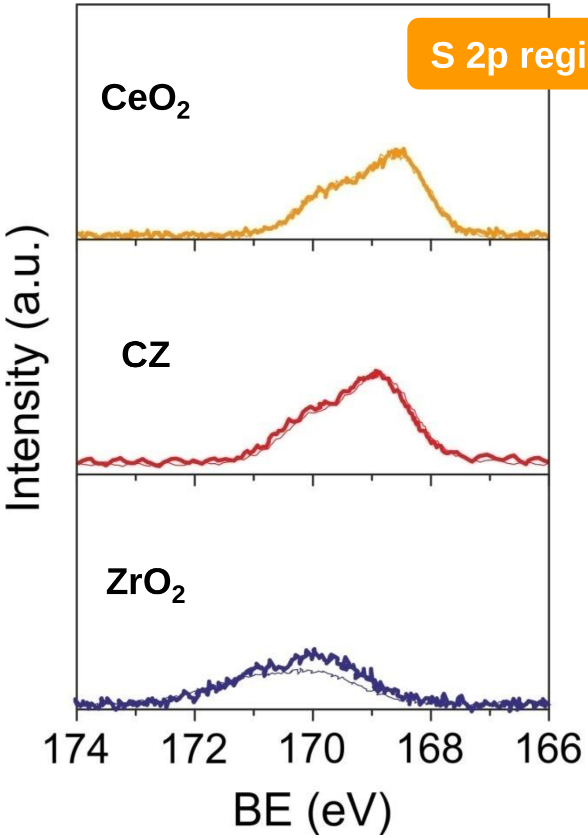
$$SO_2 + PdO \rightarrow SO_3 + Pd$$
$$SO_3 + PdO \rightarrow PdSO_4$$

Appl. Catal. B-Environ. **202** (2017), 72-83

SURFACE STUDY: SO_2 POISONING

Sulfates formation/desorption

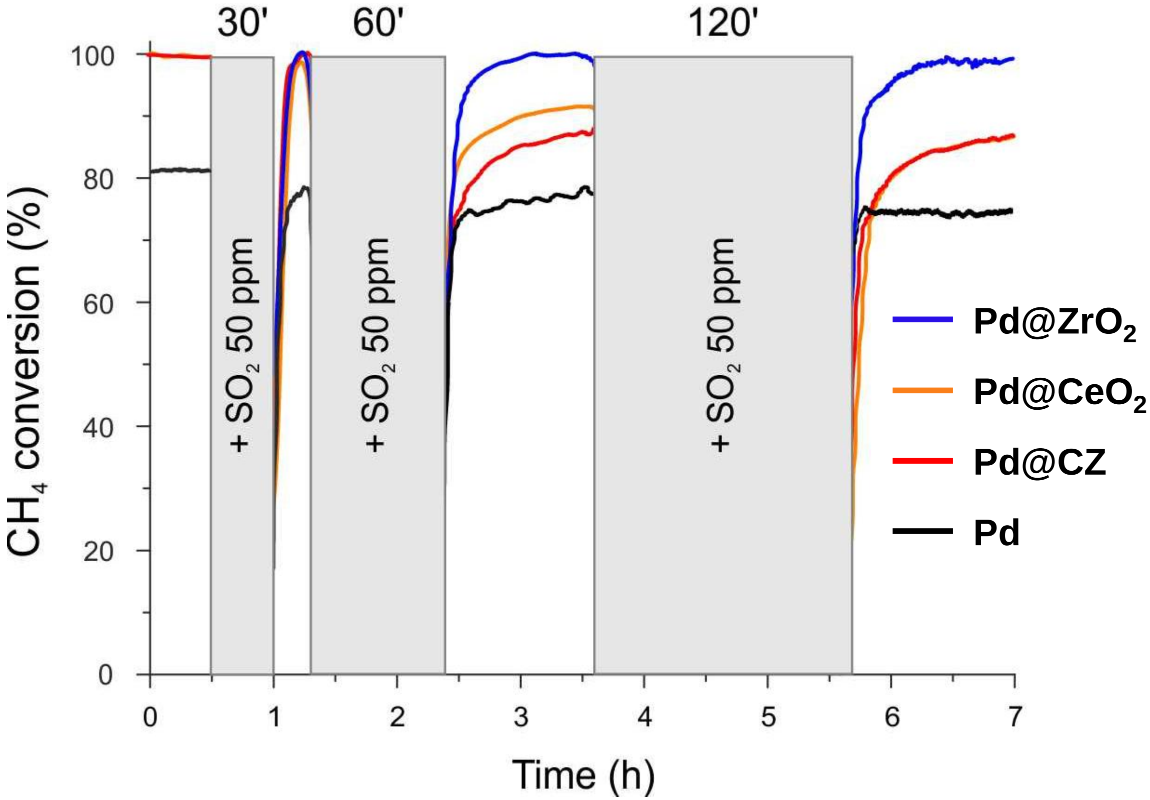
S 2p region



0.5% CH_4, 2.0% O_2, SO_2 50 ppm (if present), Ar balance, $O_2/O_{2(stoich)}$=2, GHSV = 200000 mL g^{-1} h^{-1}

$Pd@ZrO_2$ more resistant
Less sulfates formed and partial desorption

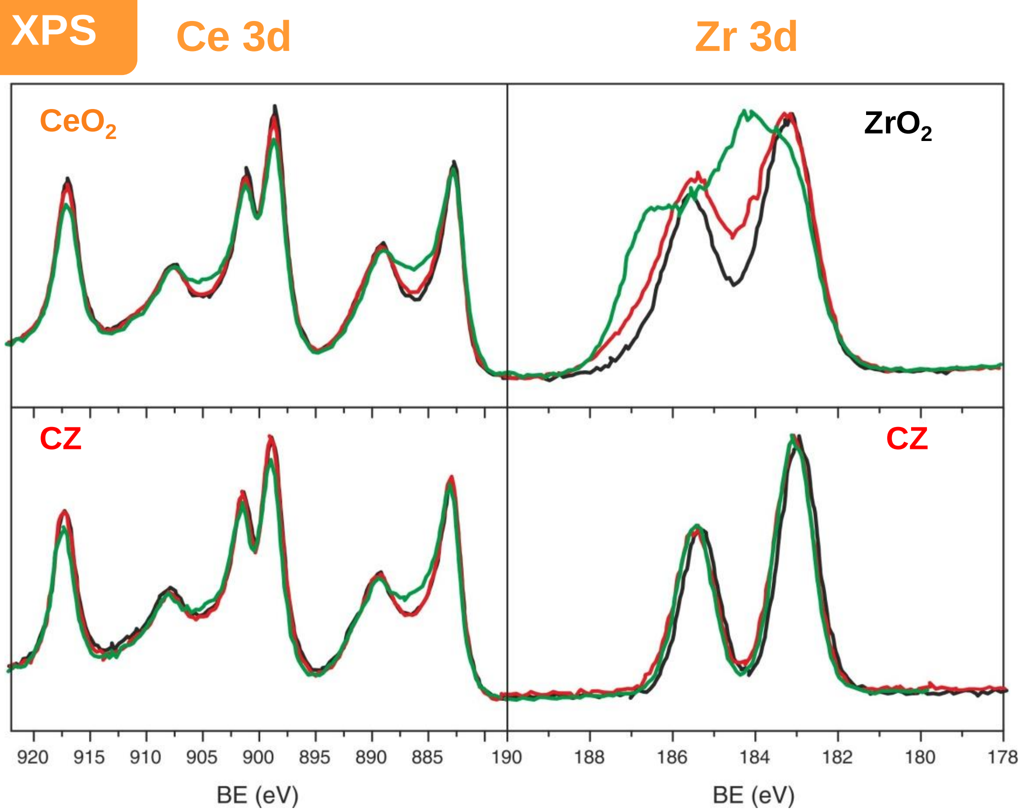
Catalytic Activity



Appl. Catal. B-Environ. **202** (2017), 72-83

Single Cations Sulfates

XPS



Pristine

500°C SO_2/dry

600°C SO_2/dry

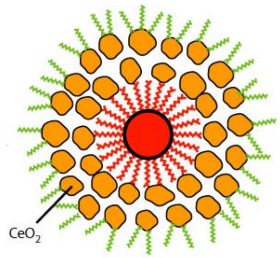
- **At 600°C: no deactivation observed**
- Modification of Ce and Zr spectra
- Zr signal not affected in CZ
- In CZ, sulfates are mostly formed on Ce

Appl. Catal. B-Environ. **202** (2017), 72-83

MEE RESEARCH ACTIVITIES

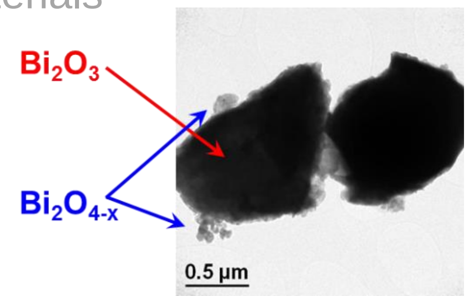
Air pollution abatement

- Three Way Catalysts
- CH_4 combustion



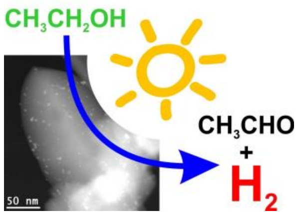
Water purification by photocatalysis

- Doped TiO_2
- Bi_2O_3-based materials
- Metal tungstates



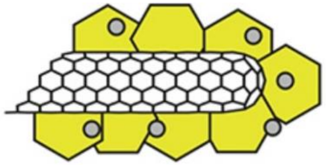
H_2 & Fuels production

- CH_4 partial oxidation
- Steam reforming of renewable compounds
- Photocatalytic reforming of oxygenated compounds
- Synthesis of valuable organic compounds



H_2 purification

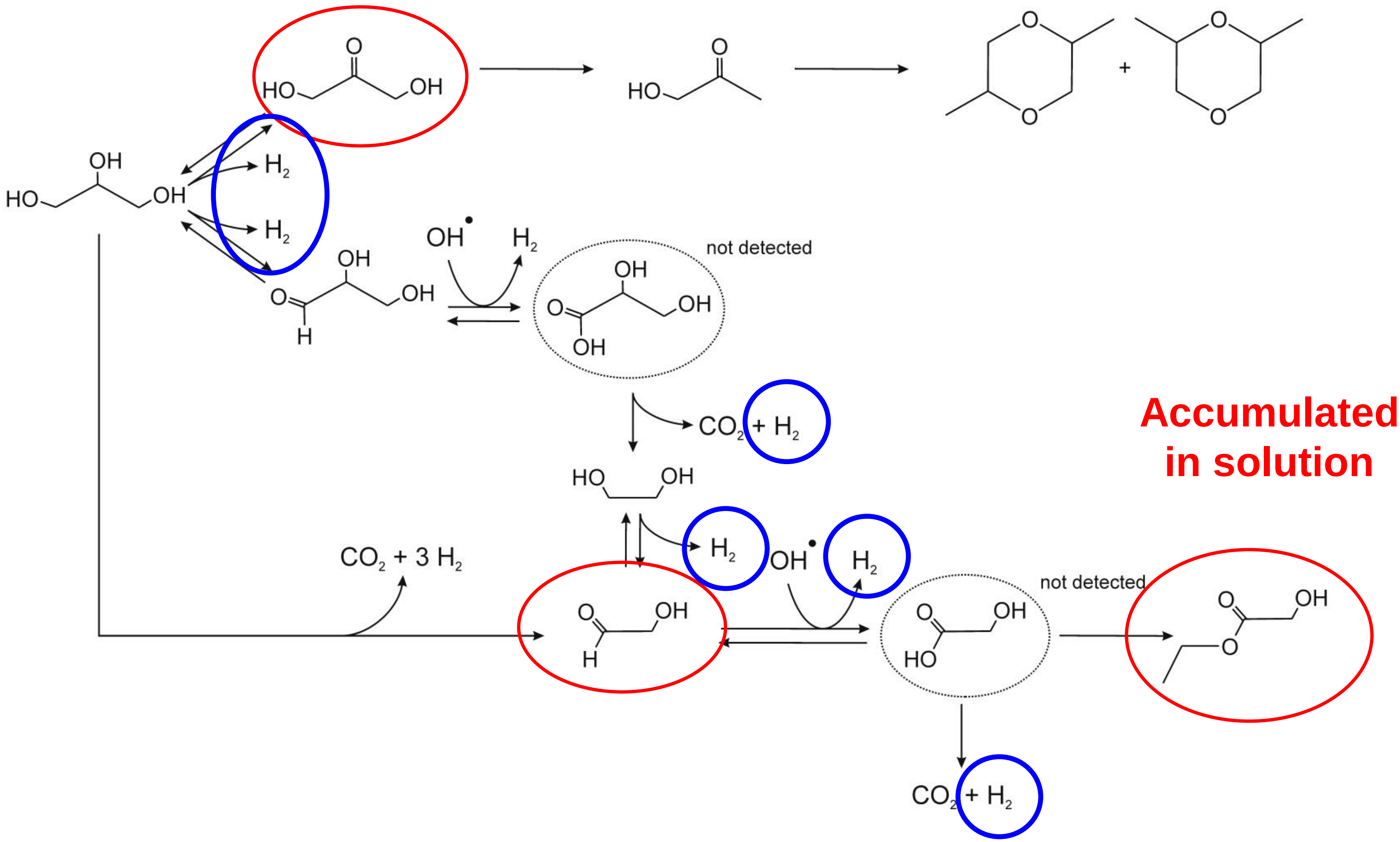
- Water Gas Shift
- Preferential Oxidation of CO



$Pd@CeO_2/MWCNT$

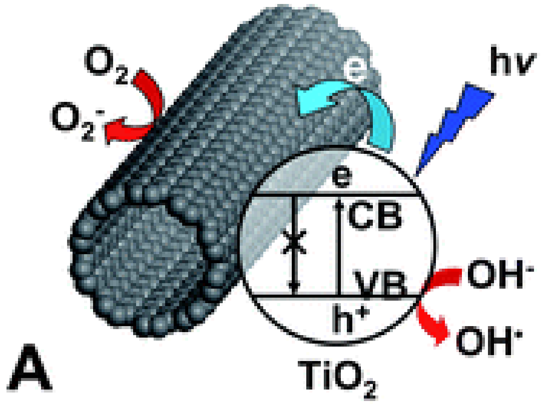
H_2 PRODUCTION FROM GLYCEROL

Possible pathway

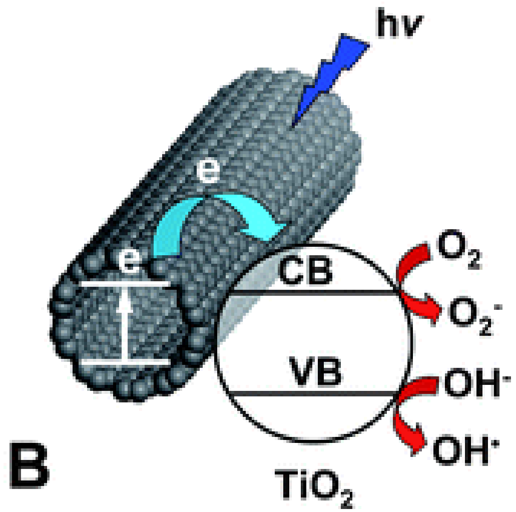


ChemCatChem **3** (2011), 574-577

Formation of hybrid materials



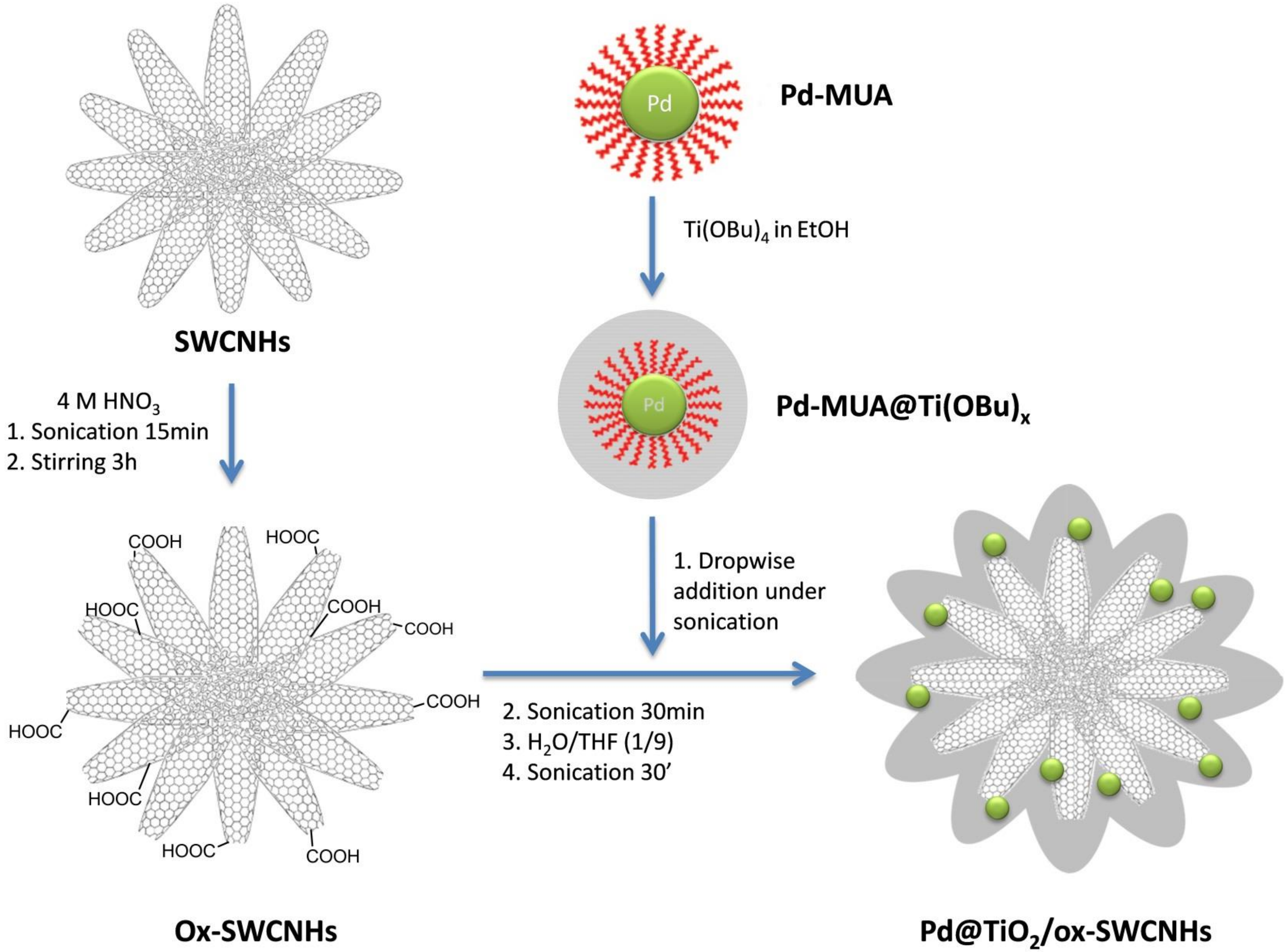
CNTs as electron sink



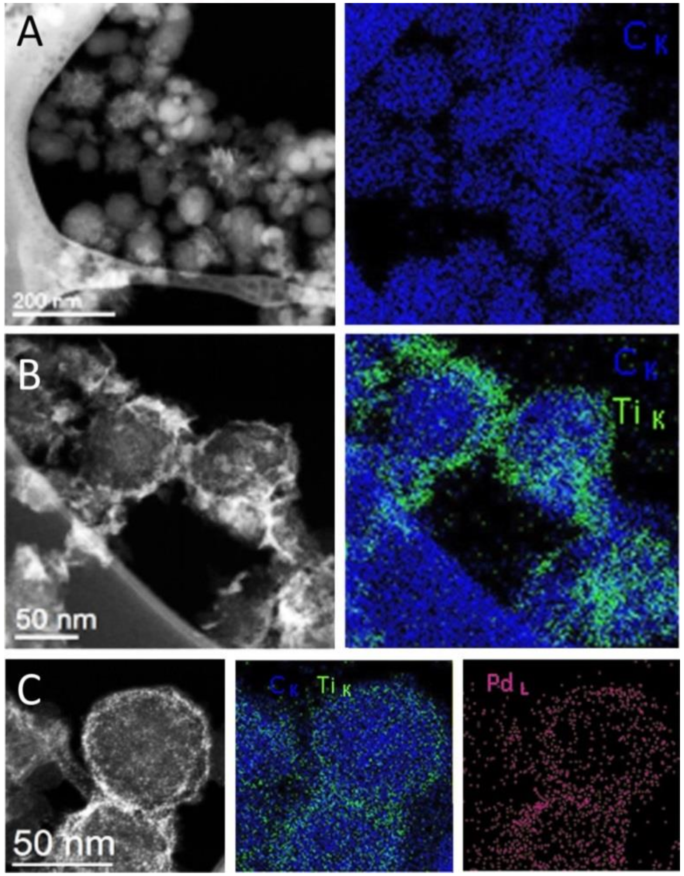
CNTs as sensitizer

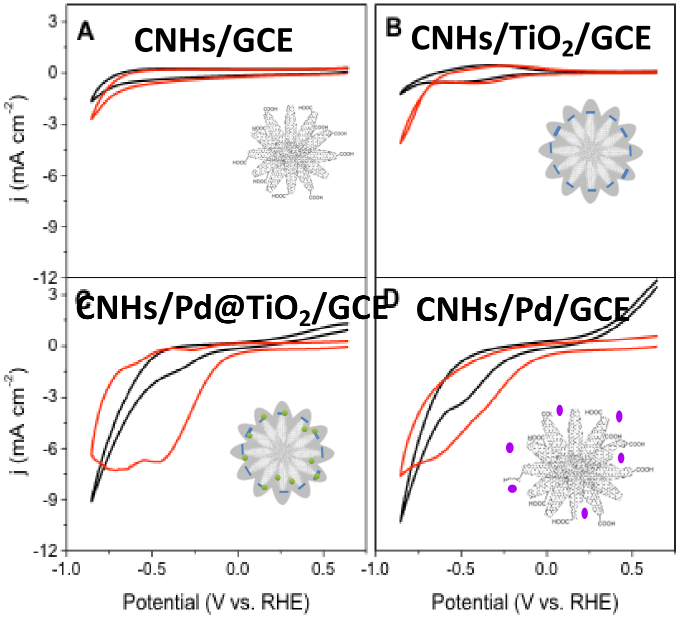
W.-D. Zhang, B. Xu, L.-C. Jiang, *J. Mater. Chem.* **20** (2010), 6383

Pd@TiO$_2$/CARBON NANOHORNS



Pd@TiO_2/CARBON NANOHORNS

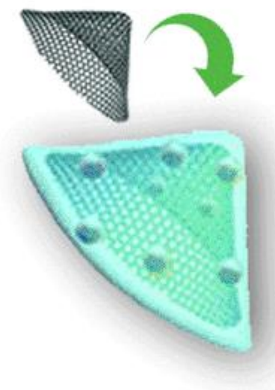


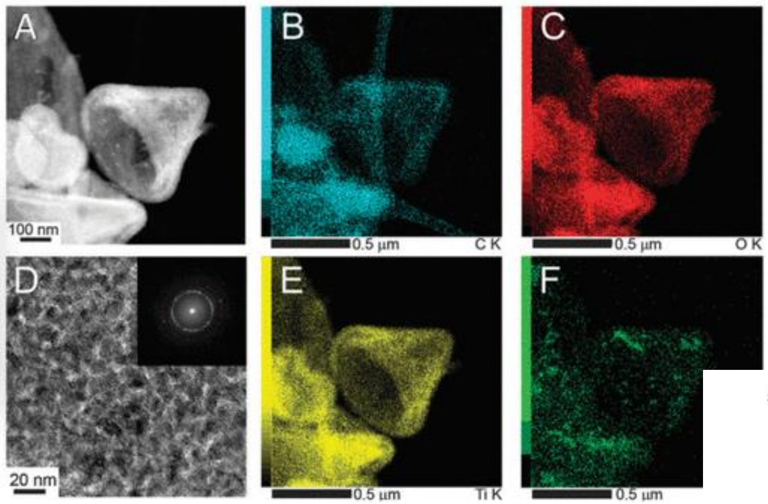


CVs measured in (—) N_2-saturated or (—) CO_2-saturated 0.10 M phosphate buffer solution pH 7.40, at 50 mV s^{-1}

Energy Environ. Sci. **2018**

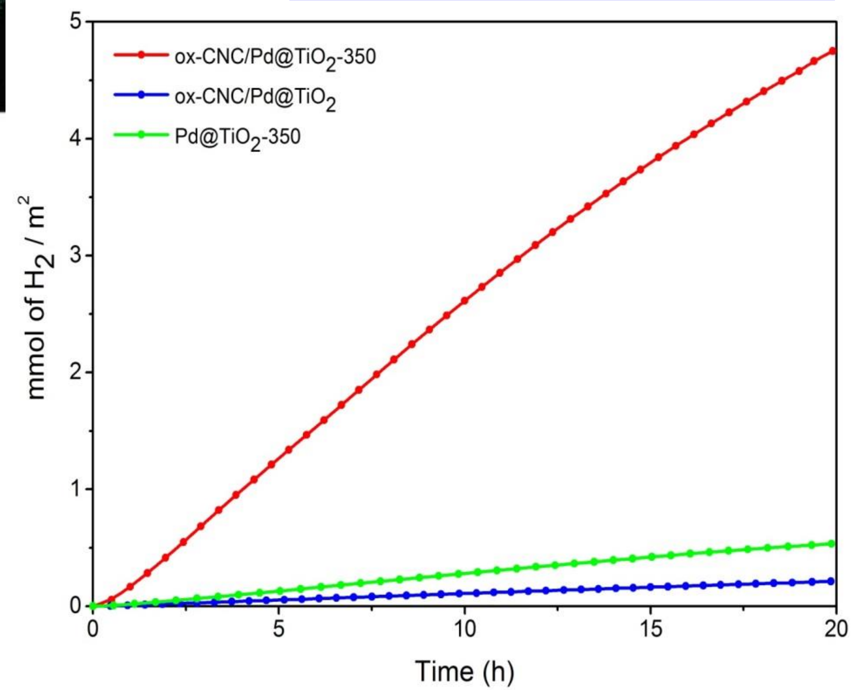
Pd@TiO_2/CARBON NANOCONES





H_2 production under Simulated sunlight

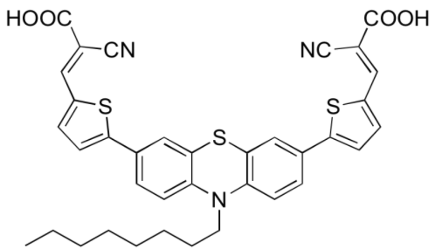
Ethanol/water solution



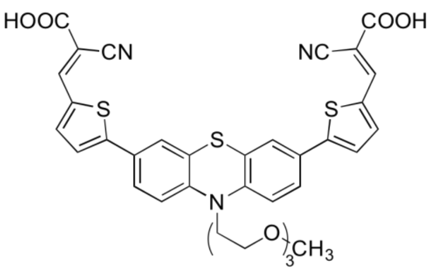
- Homogeneous coverage of CNC by porous Pd@TiO_2 shell
- Anatase phase

Montini et al. *Chem. Commun.* **52** (2016), 764-767

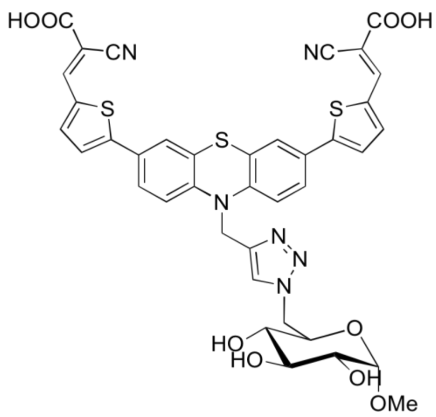
PHENOTIAZINE-BASED DYES



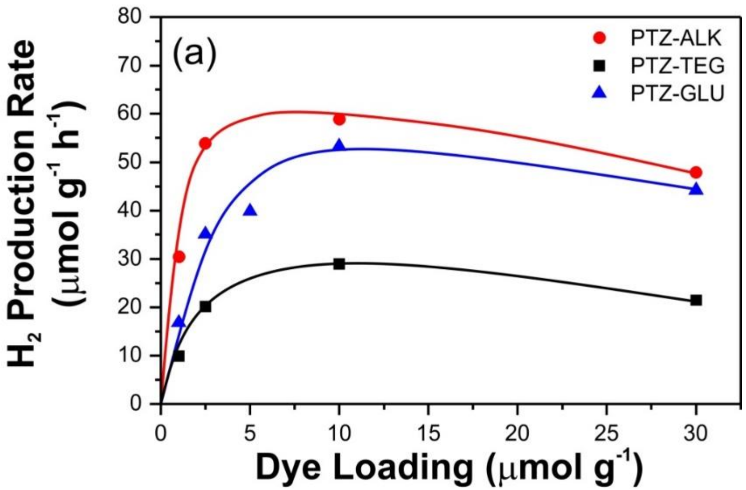
PTZ-ALK



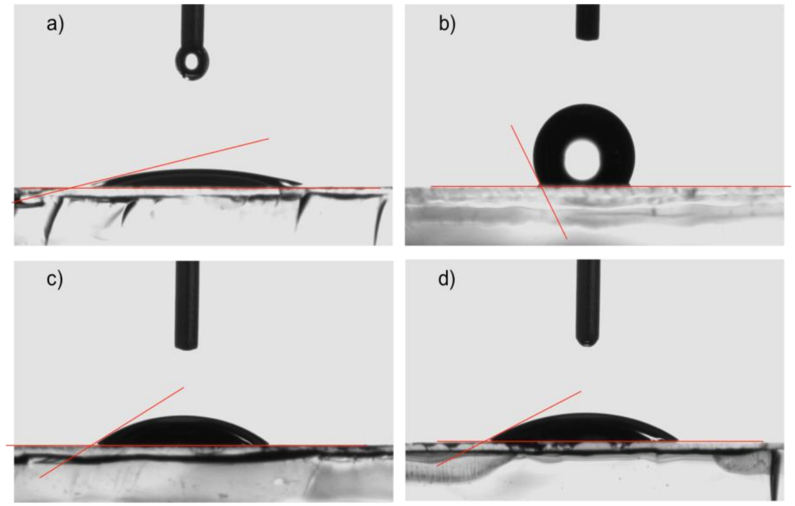
PTZ-TEG



PTZ-GLU

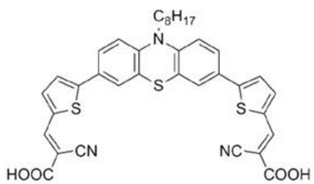


Effect of wettability

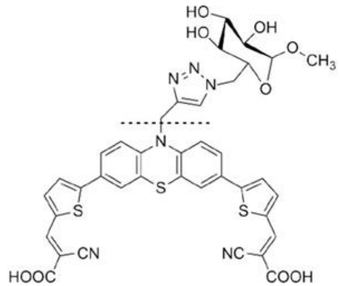


Chem. Commun. **52** (2016), 6977-6980

PHENOTIAZINE-BASED DYES

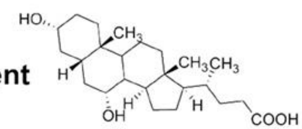


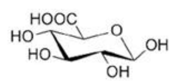
PTZ-ALK



PTZ-GLU

co-adsorbent

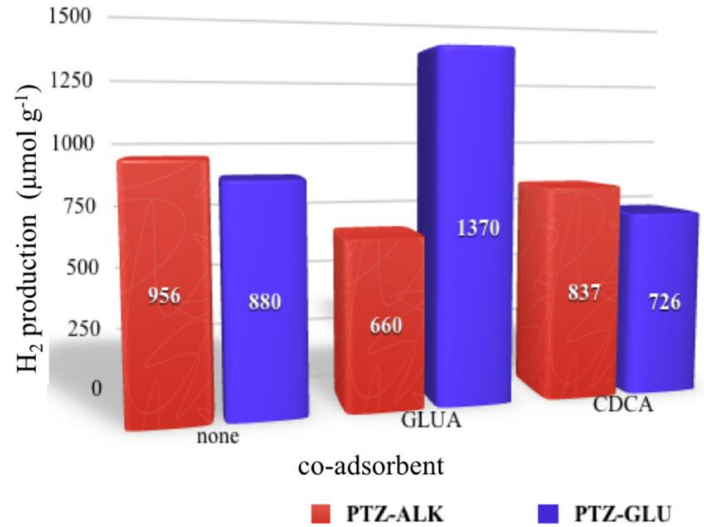


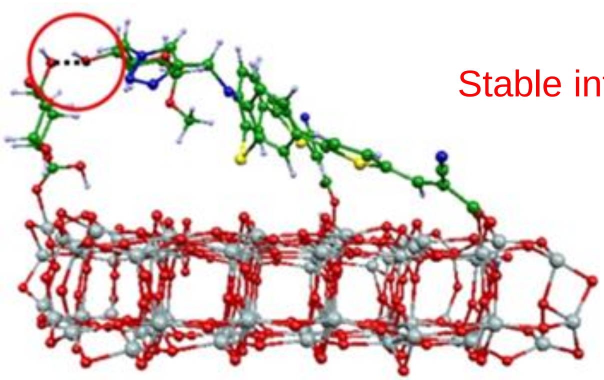


None	CDCA	GLUA
ALK	ALK - CDCA	ALK - GLUA
GLU	GLU - CDCA	GLU - GLUA

Sensitizers systems

Effect of co-adsorbents

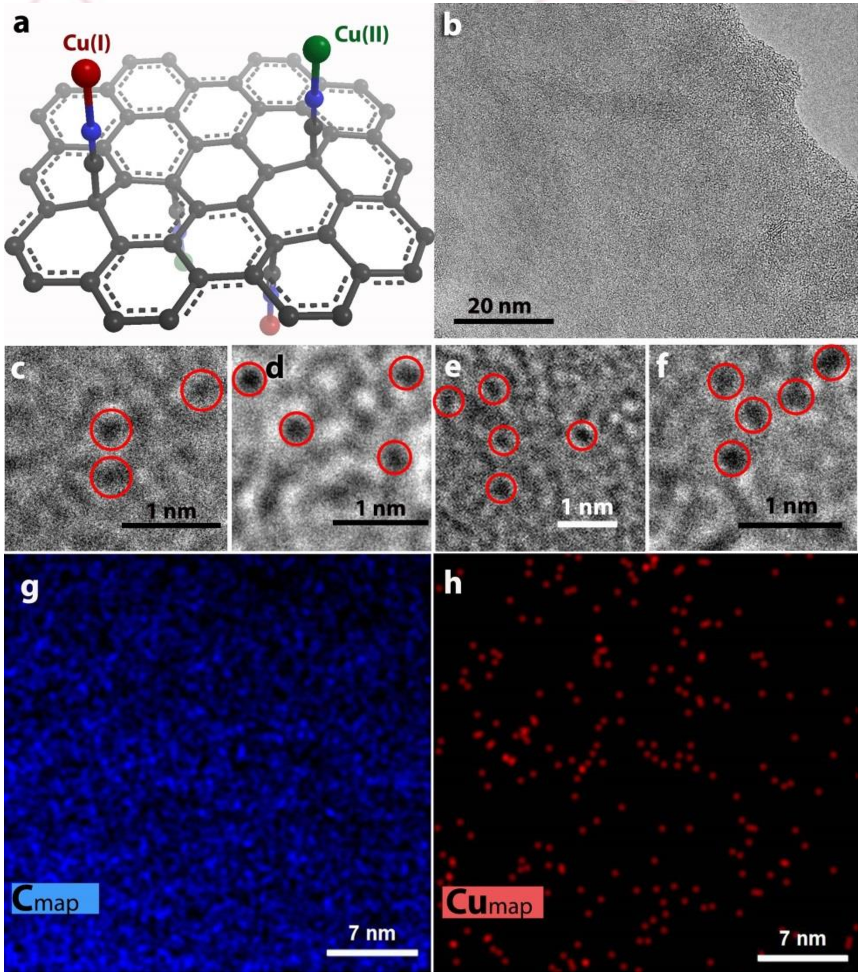




Stable interaction between PTZ-GLU and GLUA

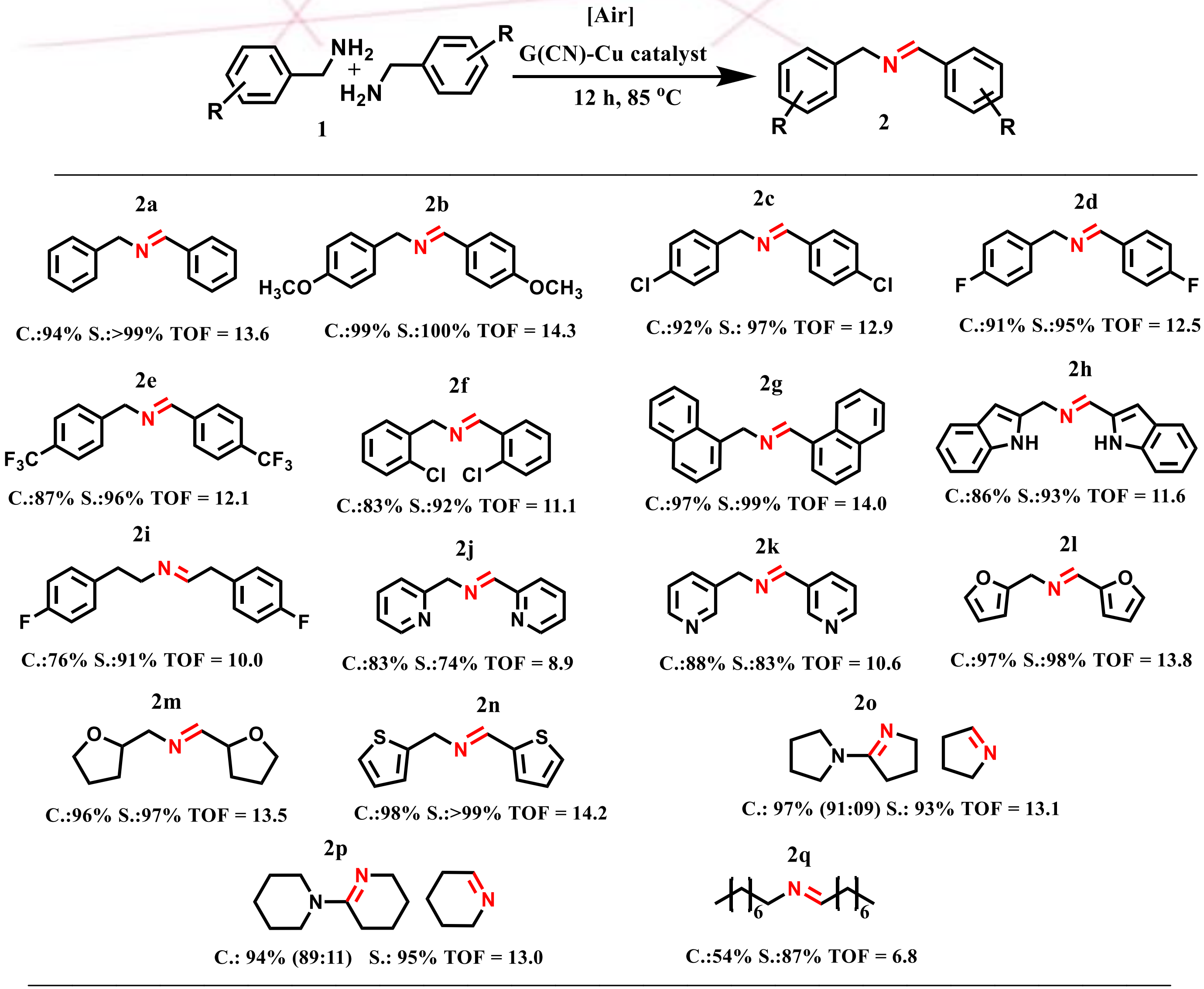
ACS Energy Lett. **3** (2018), 85-91

Single Atom Catalyst on high quality functionalized graphene



R. Zboril et al. Adv. Mater 2019

Oxidative homocoupling of substituted benzylamines



R. Zboril et al. Adv. Mater 2019

Aim of this work

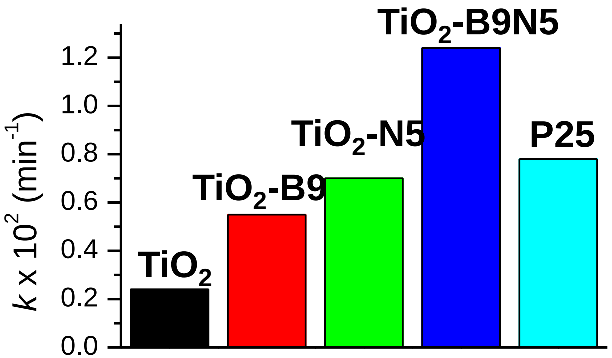
Evaluation of the effect of the doping of TiO_2 with B and N on the production of valuable chemicals:

Hydrogen

by photoreforming of aqueous solutions containing ethanol or glycerol.

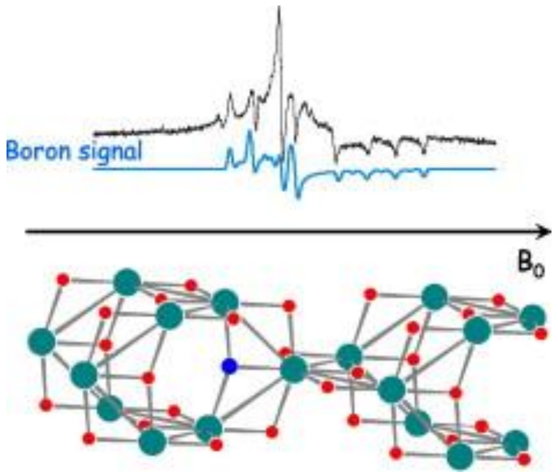
Benzimidazole

by an alternative process.



Apparent first order constant for Methyl Orange degradation

B,N



V. Gombac, L. De Rogatis, A. Gasparotto, G. Vicario, T. Montini, D. Barreca, G. Balducci, P. Fornasiero, E. Tondello and M. Graziani, *Chem. Phys.* **339** (2007) 111-123.

M. Fittipaldi, V. Gombac, T. Montini, P. Fornasiero and M. Graziani, *Inorg. Chim. Acta* **361** (2008), 3980-3987

Sol-gel method for TiO_2 supports

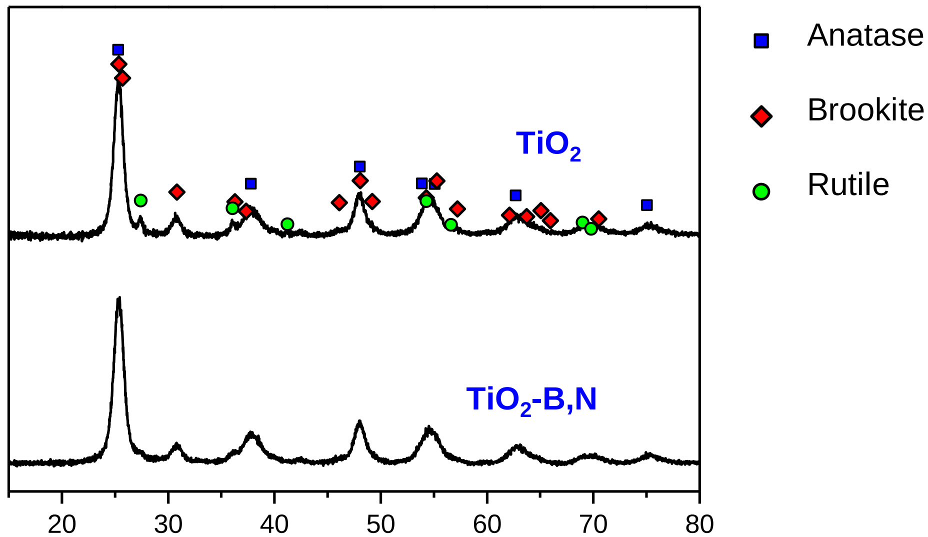
$Ti(BuO)_4 \xrightarrow[HNO_3]{EtOH / H_2O}$ gel $\longrightarrow$ Drying $\longrightarrow$ Calcination **TiO_2**

$Ti(BuO)_4$ + H_3BO_3 + H_2NCONH_2 $\xrightarrow[HNO_3]{EtOH / H_2O}$ gel $\longrightarrow$ Drying $\longrightarrow$ Calcination

TiO_2-B,N

B / Ti = 0.09
N / Ti = 0.05

Characterization of the supports



- Mixture of polymorphs
- High surface area
- Improved by B,N doping

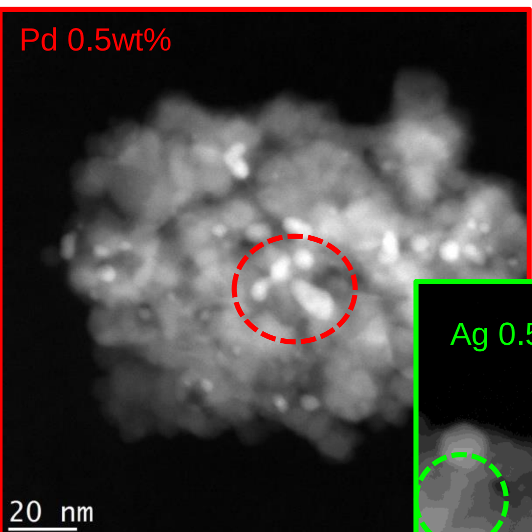
	Composition (wt%)			Crystallite size (nm)			Surface area (m^2 g^{-1})
	Anatase	Brookite	Rutile	Anatase	Brookite	Rutile	
TiO_2	64	28	8	11	11	32	80
TiO_2-B,N	68	26	6	8	7	12	138

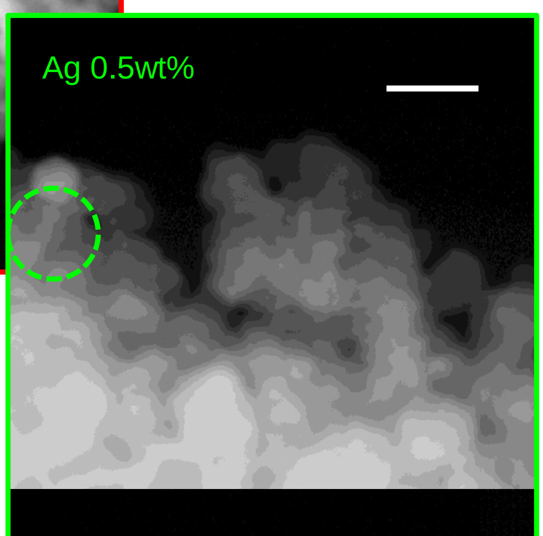
Deposition of the metal phase

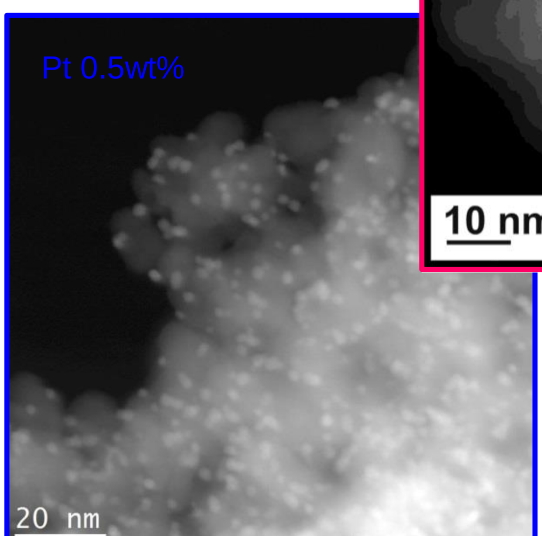
Metal photodeposition

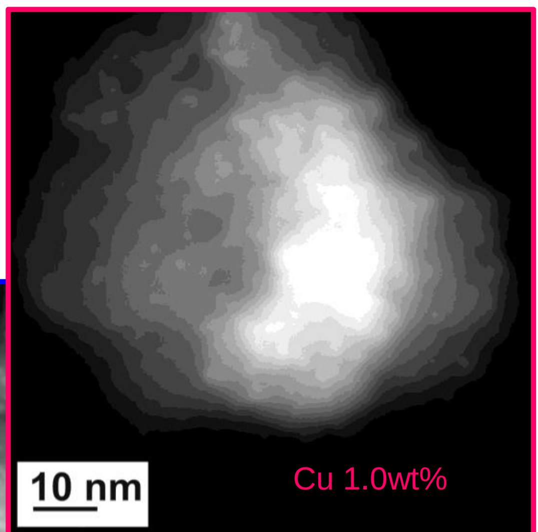
Support + metal nitrate —(50% water- 50% ethanol / UV-vis irradiation)→ **Metal/TiO_2**, **Metal/TiO_2-B,N**

HAADF-STEM



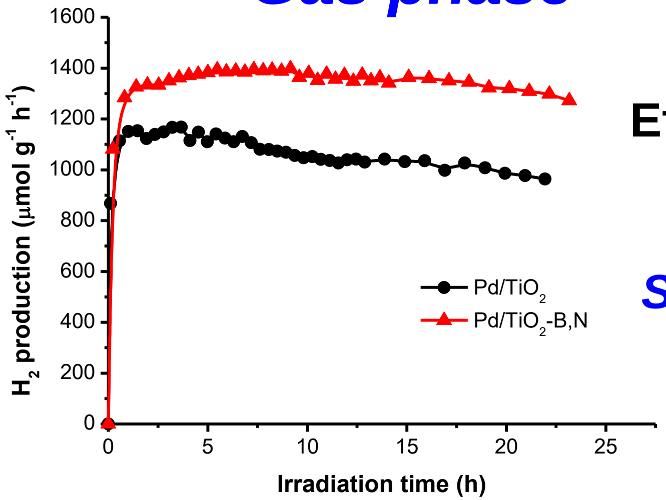






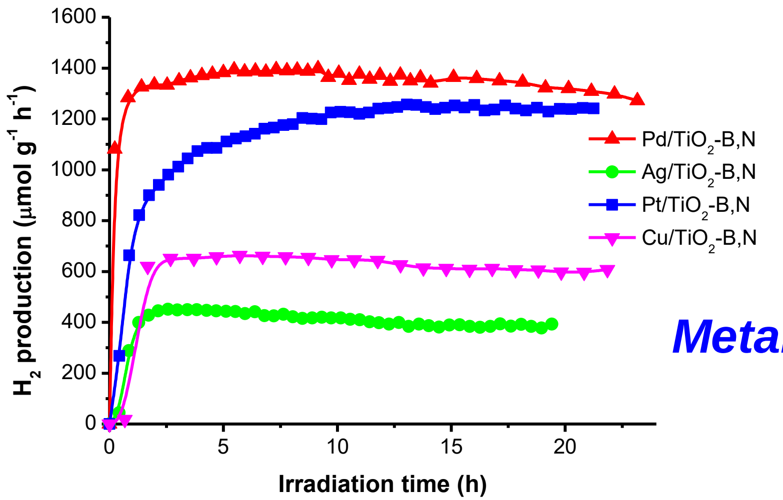
H_2 production from ETHANOL

Gas phase

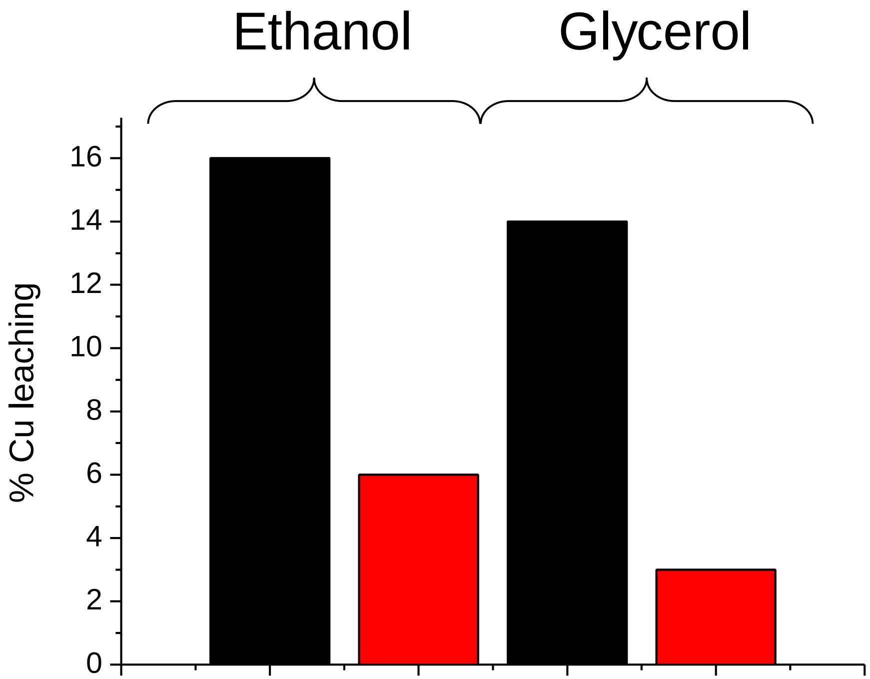


Effect of:

Support



Metal



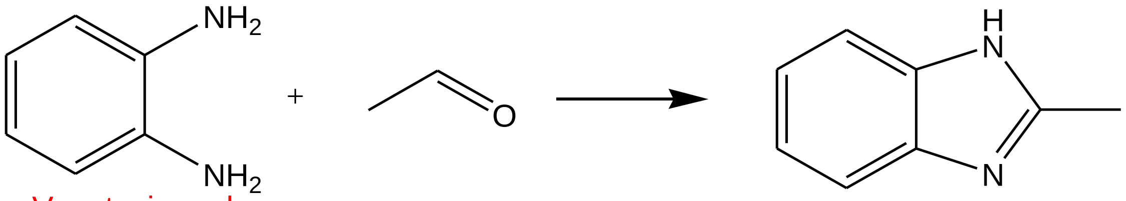
Cu/TiO_2

Cu/TiO_2-B,N

- Doping TiO_2, leaching is significantly reduced
- More stable performances for TiO_2-B,N supported catalysts

Synthesis of benzimidazole

Conventional synthesis:

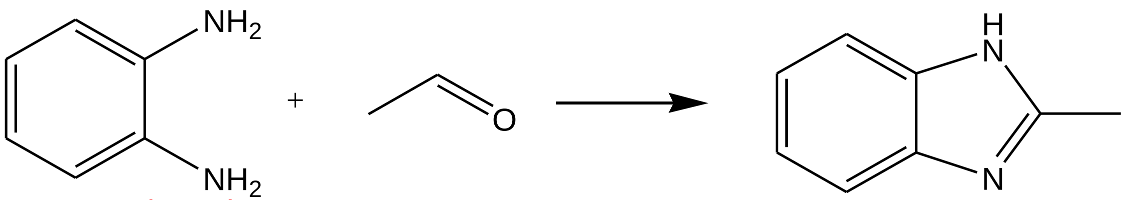


Very toxic and carcinogenic

- T = 100 – 200 °C
- Strong acidic conditions
- Strong oxidants

Synthesis of benzimidazole

Conventional synthesis:



Very toxic and carcinogenic

- T = 100 – 200 °C
- Strong acidic conditions
- Strong oxidants

Communications

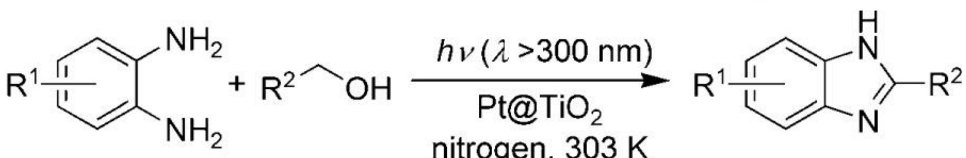
Heterogeneous Catalysis

DOI: 10.1002/anie.200906573

One-Pot Synthesis of Benzimidazoles by Simultaneous Photocatalytic and Catalytic Reactions on Pt@TiO_2 Nanoparticles**

Yasuhiro Shiraishi, Yoshitsune Sugano, Shunsuke Tanaka, and Takayuki Hirai*

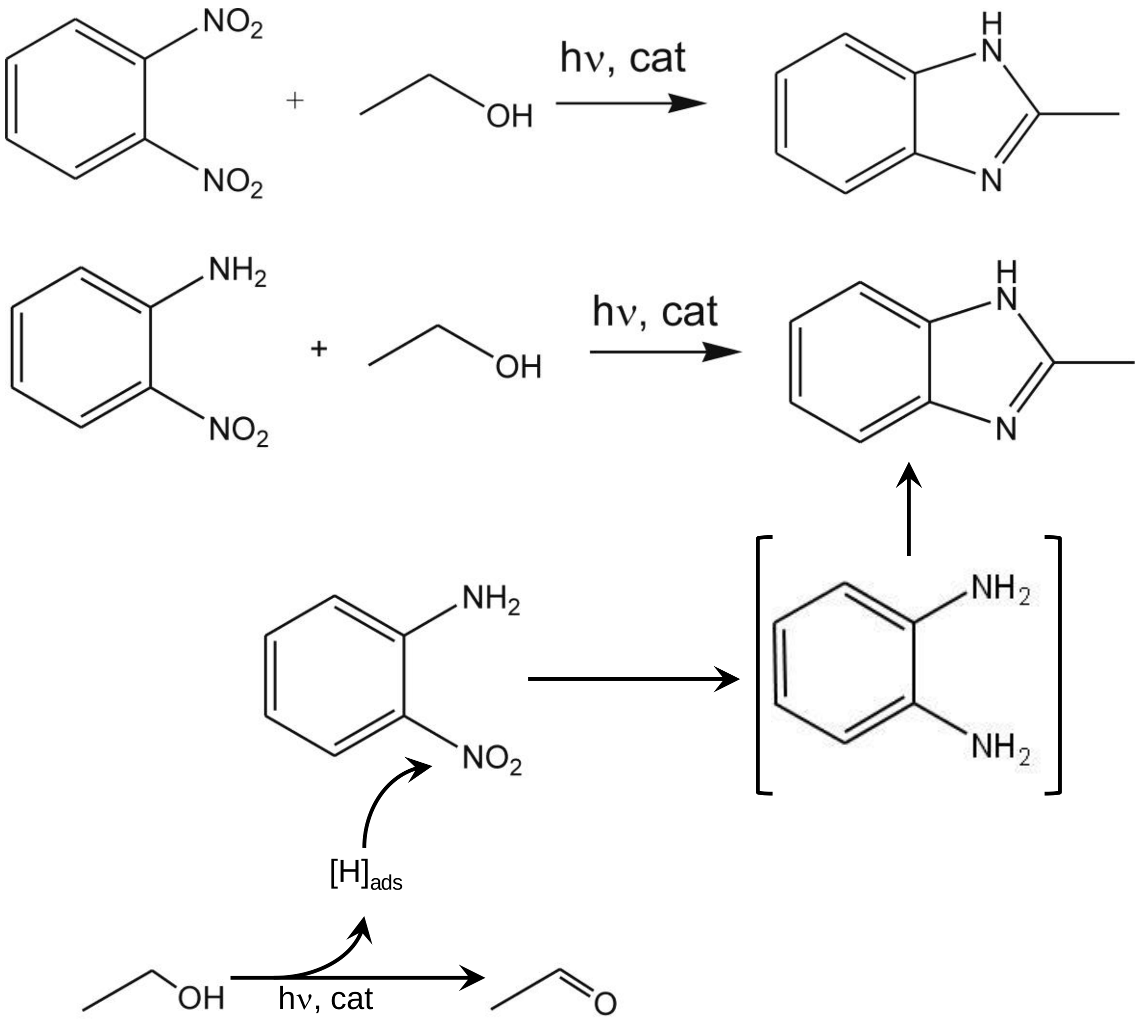
Angew. Chem. Int. Ed. **2010**, *49*, 1656–1660



Scheme 1. One-pot synthesis of benzimidazole using a Pt@TiO_2 catalyst under photoirradiation.

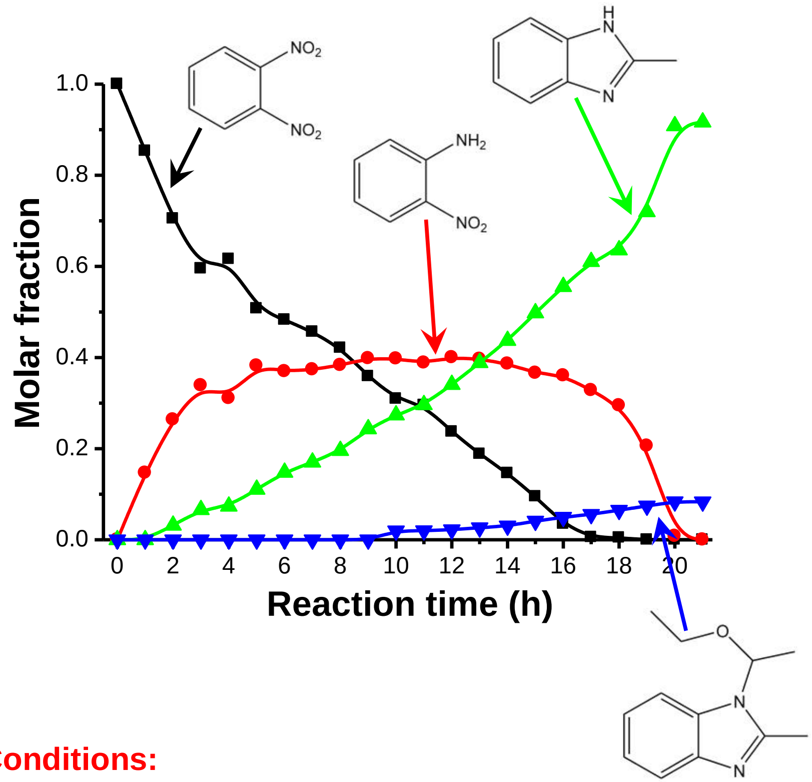
Synthesis of benzimidazole

Alternative processes:



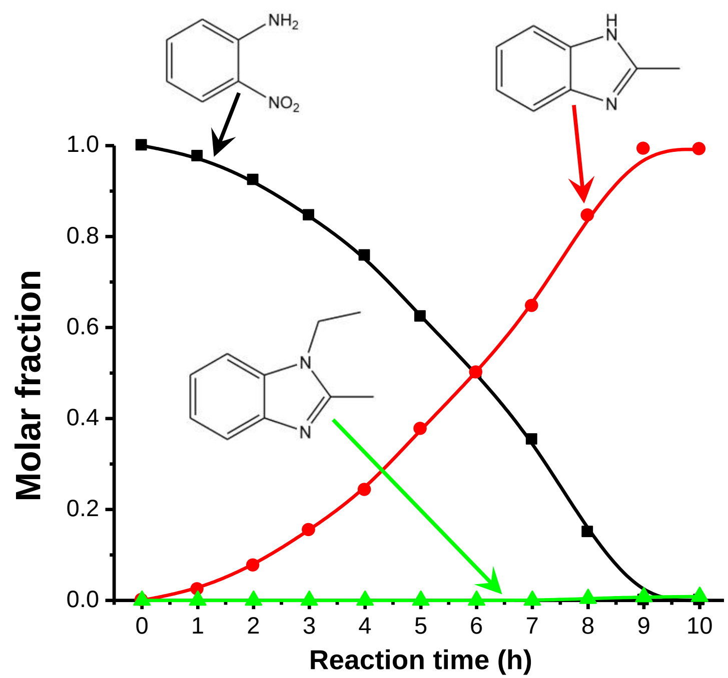
- Less toxic reagents
- Renewable and cheap solvent

Synthesis of 2-methylbenzimidazole

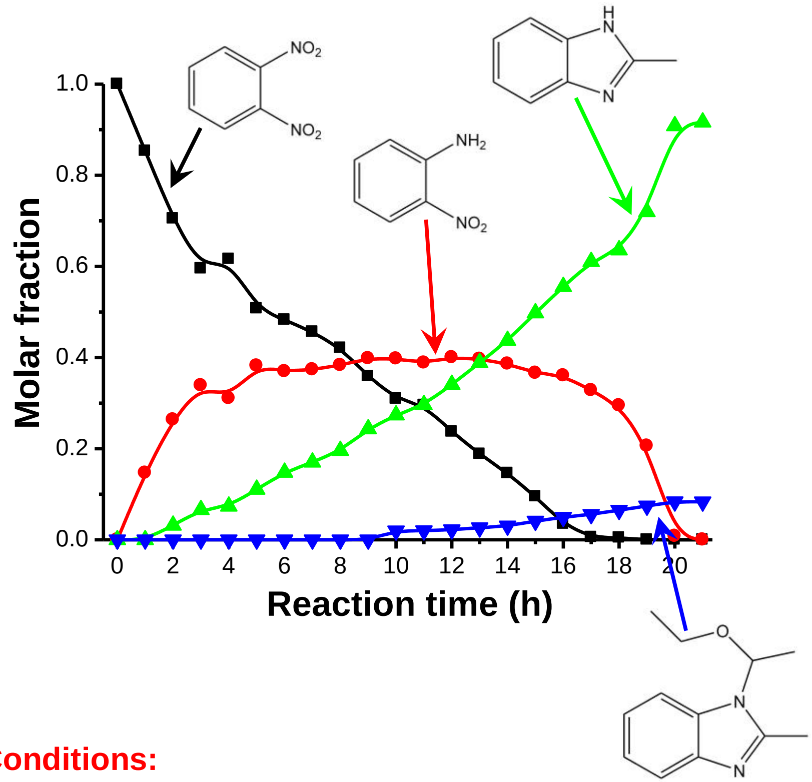


Conditions:

- 60 mL DNB/NA 2mM in EtOH 96%
- 150 mg Pd/TiO_2-B,N
- Ar flow, 30°C
- Simulated sunlight irradiation



Synthesis of 2-methylbenzimidazole



Conditions:
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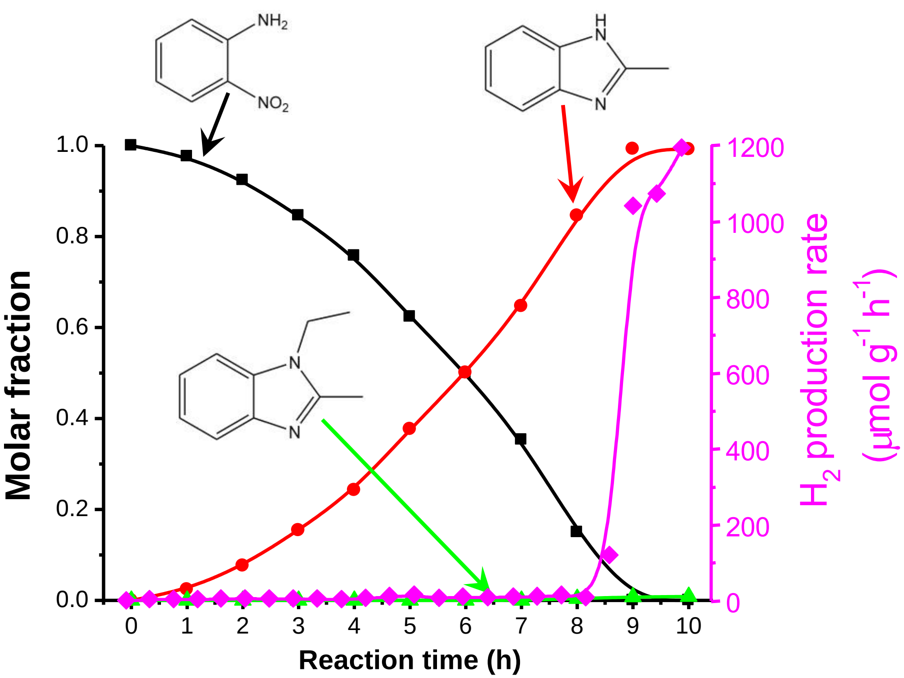
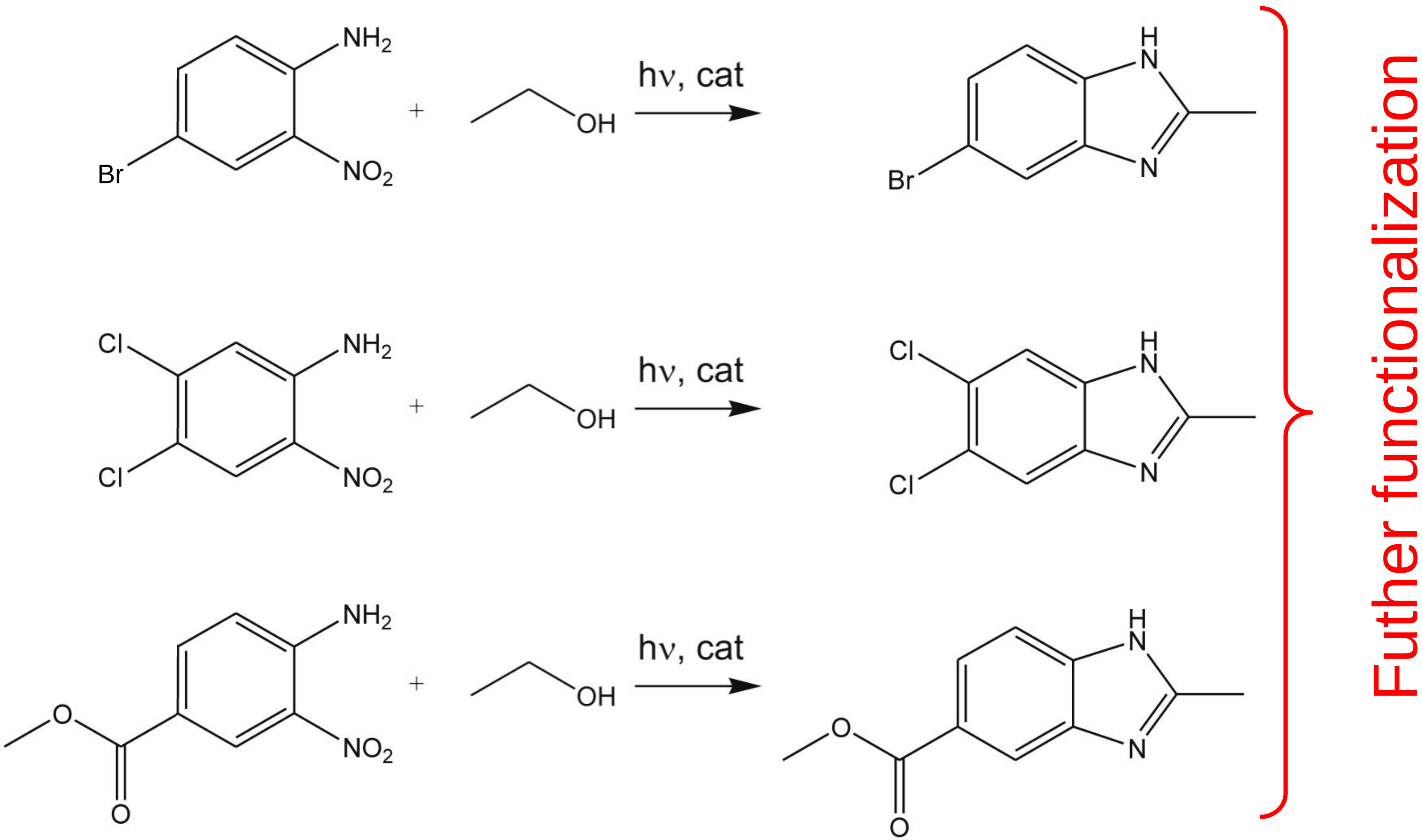
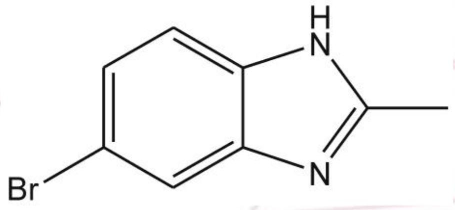
- Simulated sunlight irradiation



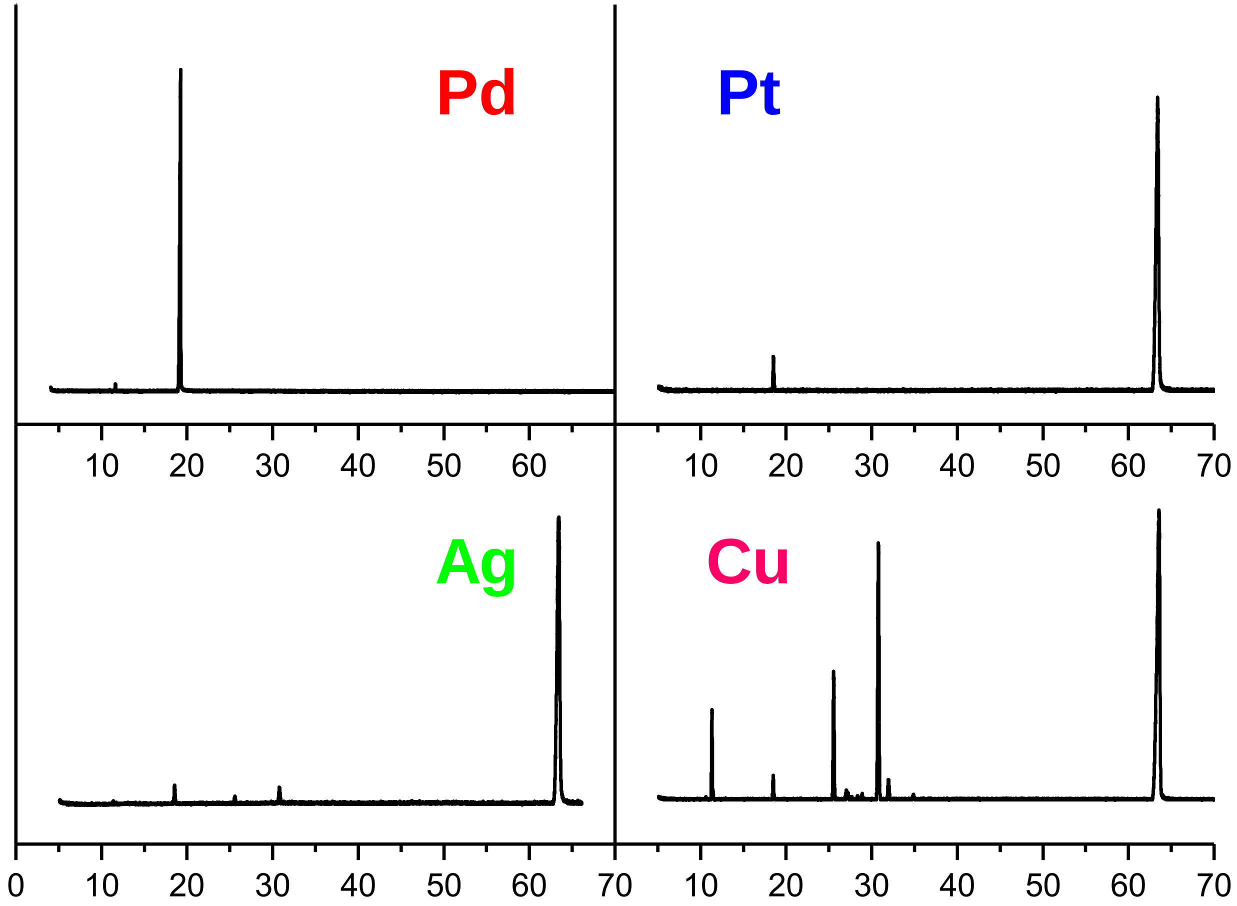
Substituted 2-methylbenzimidazole



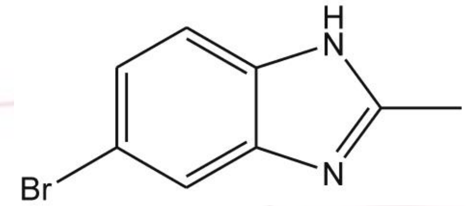
Bromo derivate



GC/MS analysis

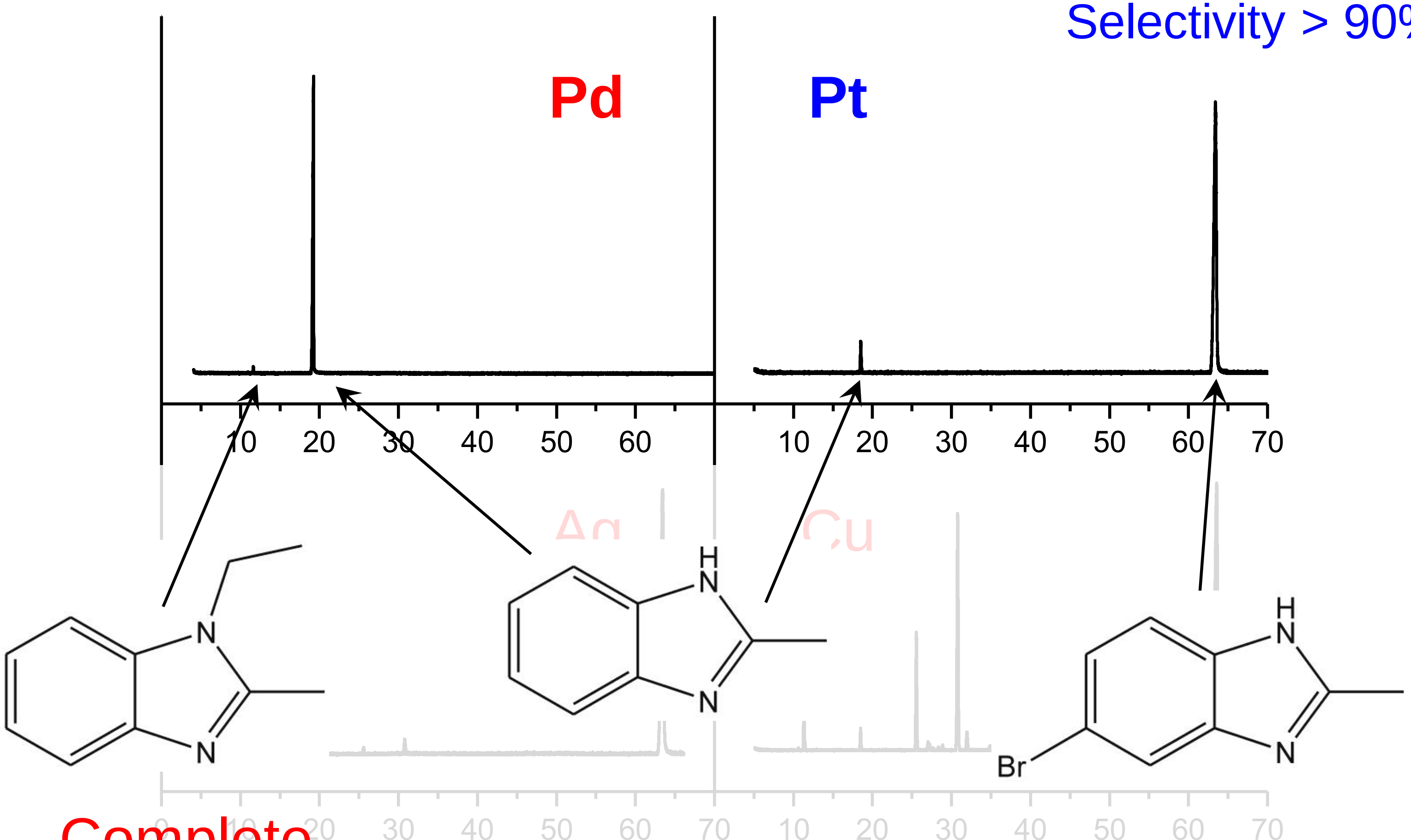


Bromo derivate



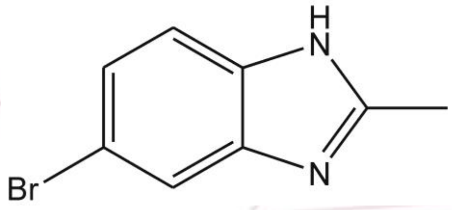
GC/MS analysis

Selectivity > 90%

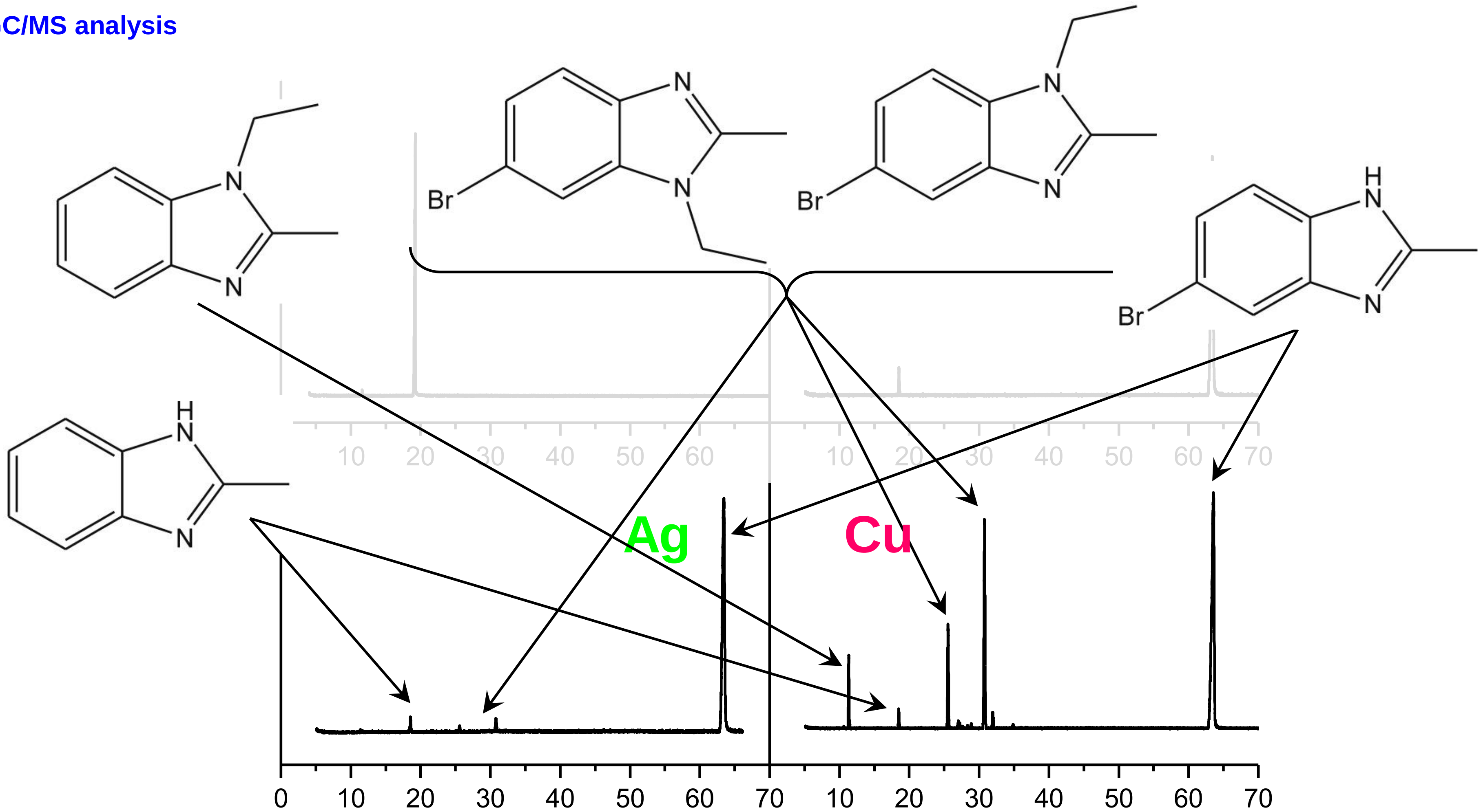


Complete hydrodebromination

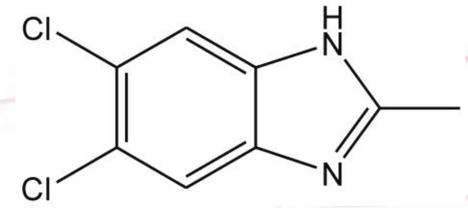
Bromo derivate



GC/MS analysis

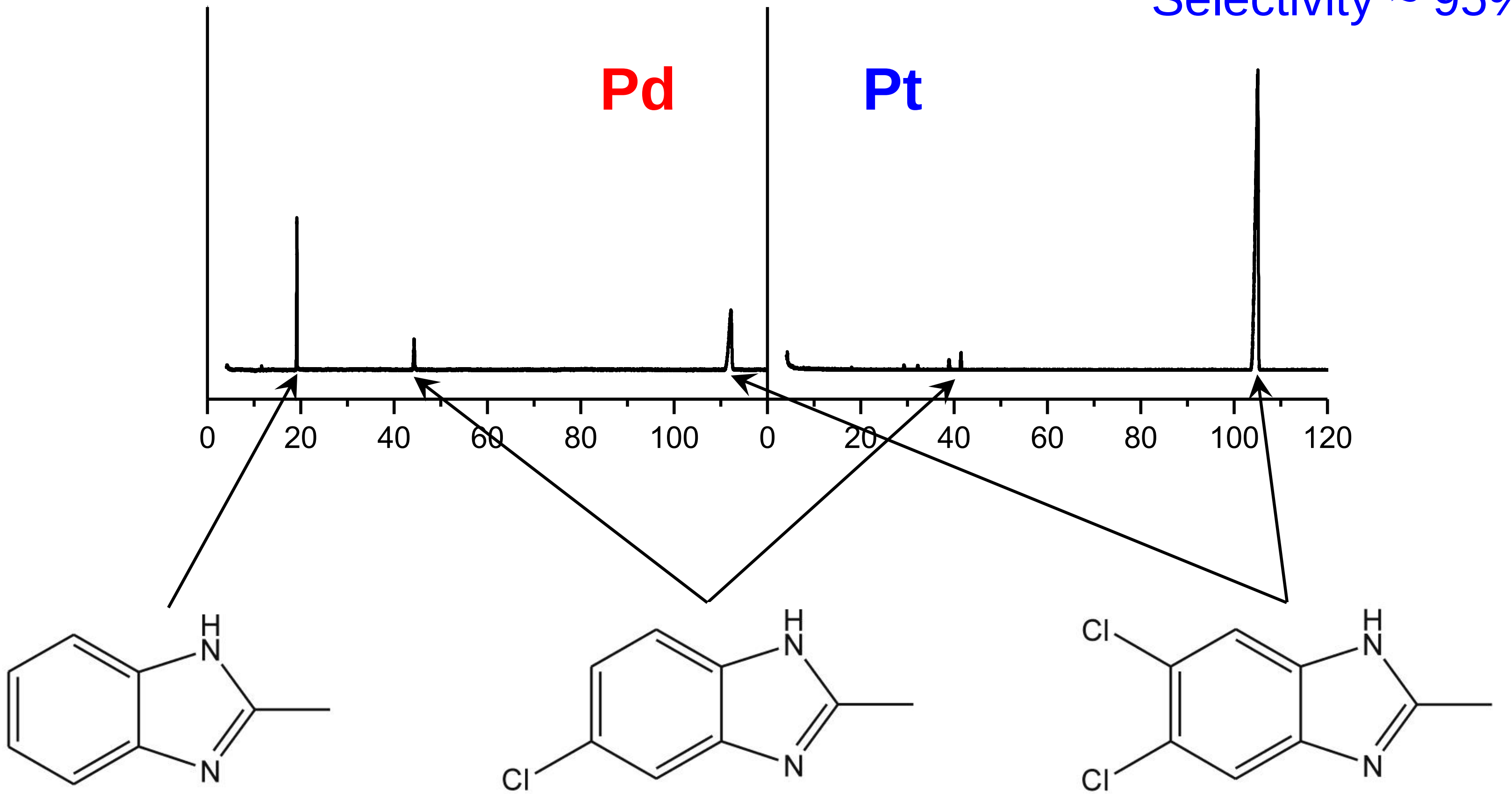


Chloro derivate

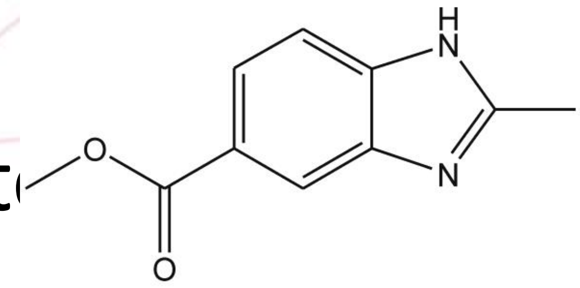


GC/MS analysis

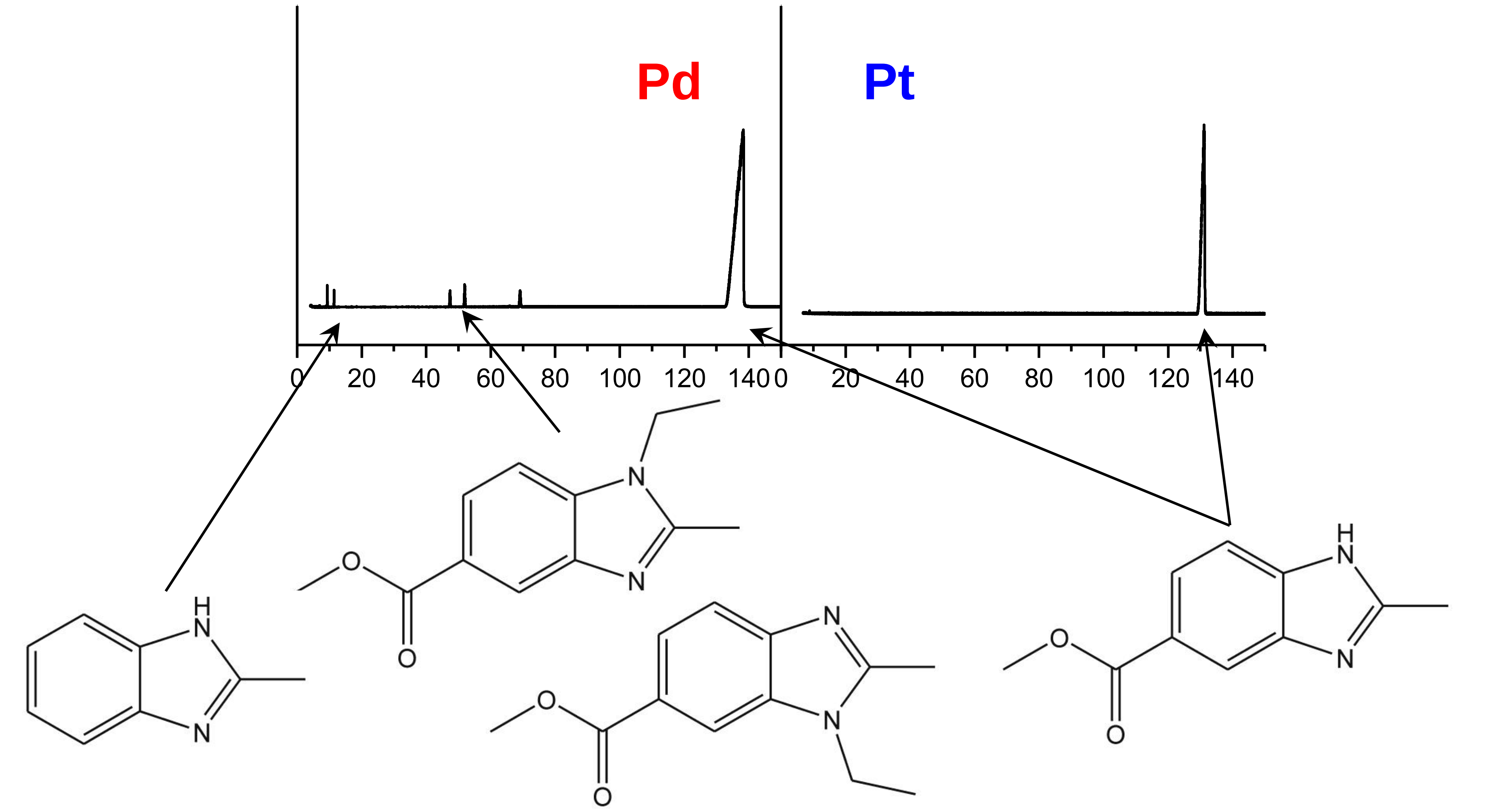
Selectivity ~ 95%



Methyl ester derivat



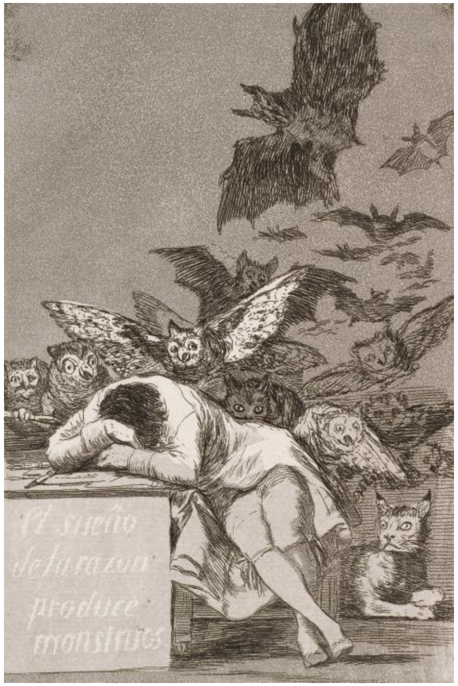
GC/MS analysis



ACKNOWLEDGEMENTS

Group members:
Prof. Paolo Fornasiero, Dr. Michele Melchionna
Dr. Valentina Gombac, Dr. Manuela Bevilacqua
Dr. Matteo Monai, Dr. Alessandro Beltram

Prof. Mauro Graziani
1936 – 2019



The sleep of reason produces monsters
Francisco Goya (1799)