The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

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2269-9

Workshop on New Materials for Renewable Energy

17 - 21 October 2011

Photocatalytic H2 and added-value byproducts: The role of metal oxide systems in their synthesis from liquid oxygenates

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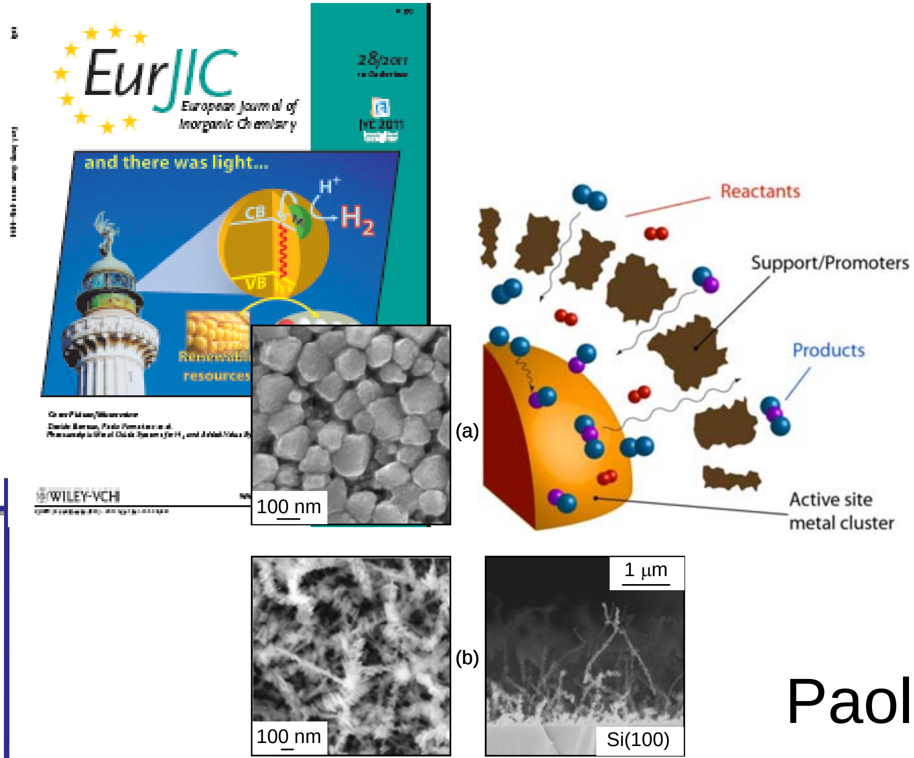
Italy

Photocatalytic H_2 and added-value byproducts:

the role of metal oxide systems in their synthesis from liquid oxygenates



Paolo Fornasiero

University of Trieste

Workshop on New Materials for Renewable Energy
Trieste 17-10-2011

Outline

1. Introduction: motivation and context

2. Nanostructured powder materials

    - CuO_x@TiO_2

    - CuO_x or Pd on B,N co-doped TiO_2

    - Pt, Au and Pt-Au on TiO_2

3. Supported nanoarchitectures

    - CuO and Cu_2O

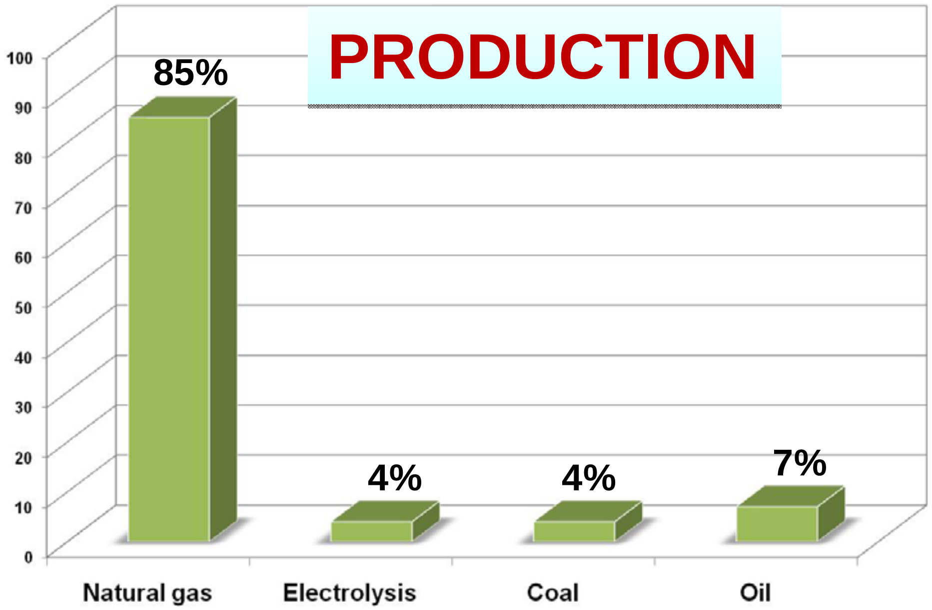
    - Bare and Au doped CuO_x/TiO_2

    - Bare and F- doped Co_3O_4

    - Ag/ZnO

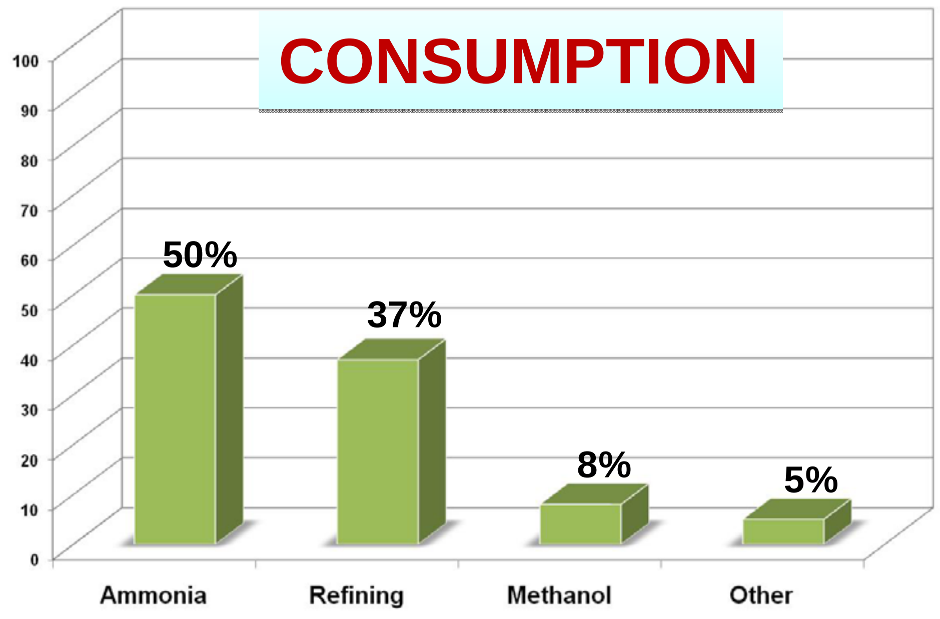
4. Perspectives

Motivation of H_2 production



Current world production
~ 500 billion Nm^3/yr

Currently, most of the CO_2 associated with H_2 production is released to atmosphere



Hydrogen production strategies and photo-catalysis

Steam reforming (methane, oxygenates ….)

Partial oxidation reaction (methane, oxygenates …)

Auto-thermal reforming (methane, oxygenates …)

Aqueous phase reforming (oxygenates,…)

Sustainability

Electrolysis by renewable energy

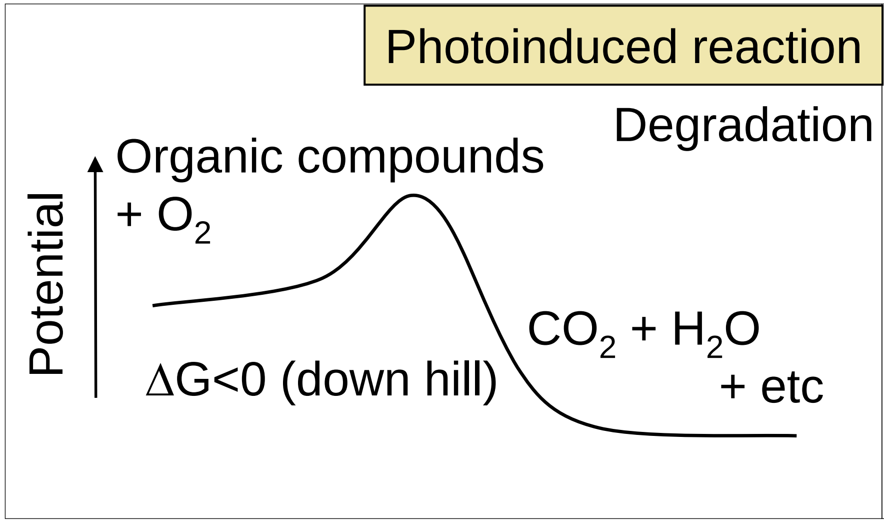
Gasification (biomass….)

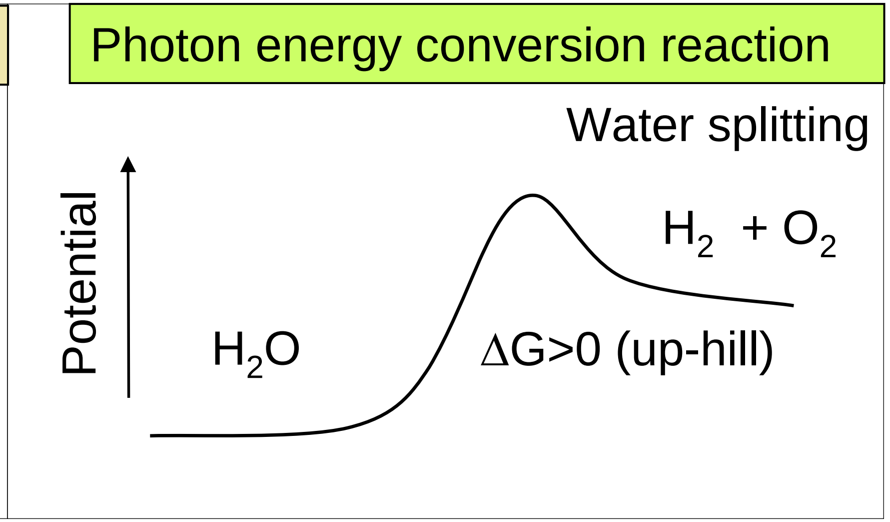
Bacteria (biomass…)

Thermo-chemical water splitting

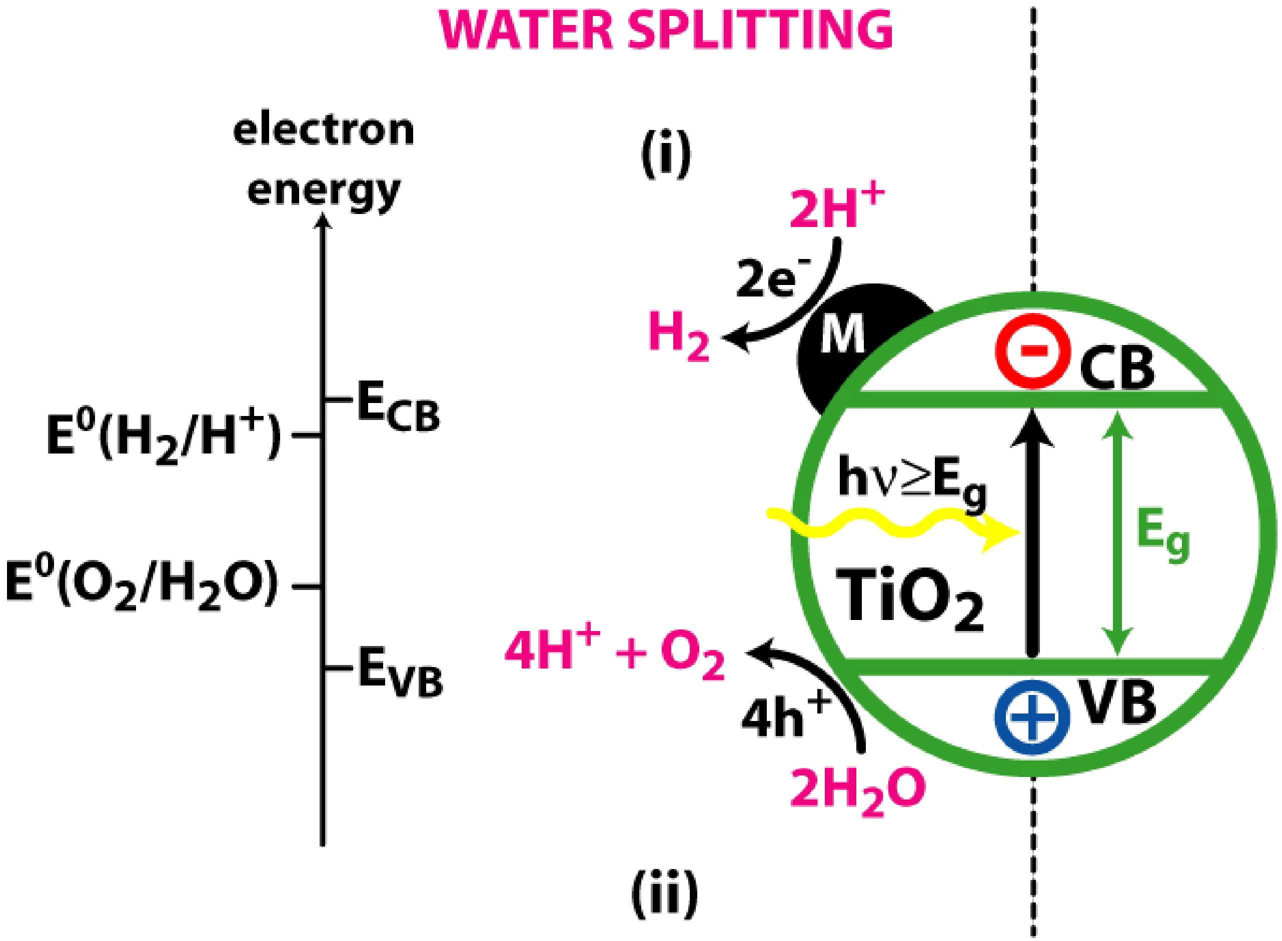
Photo-catalytic reforming of oxygenate

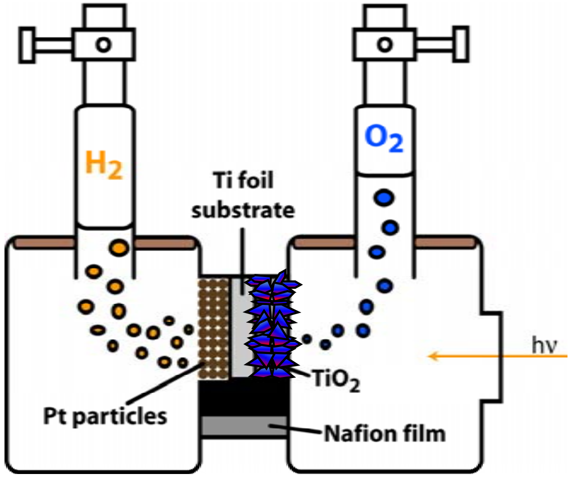
Photo-catalytic water splitting





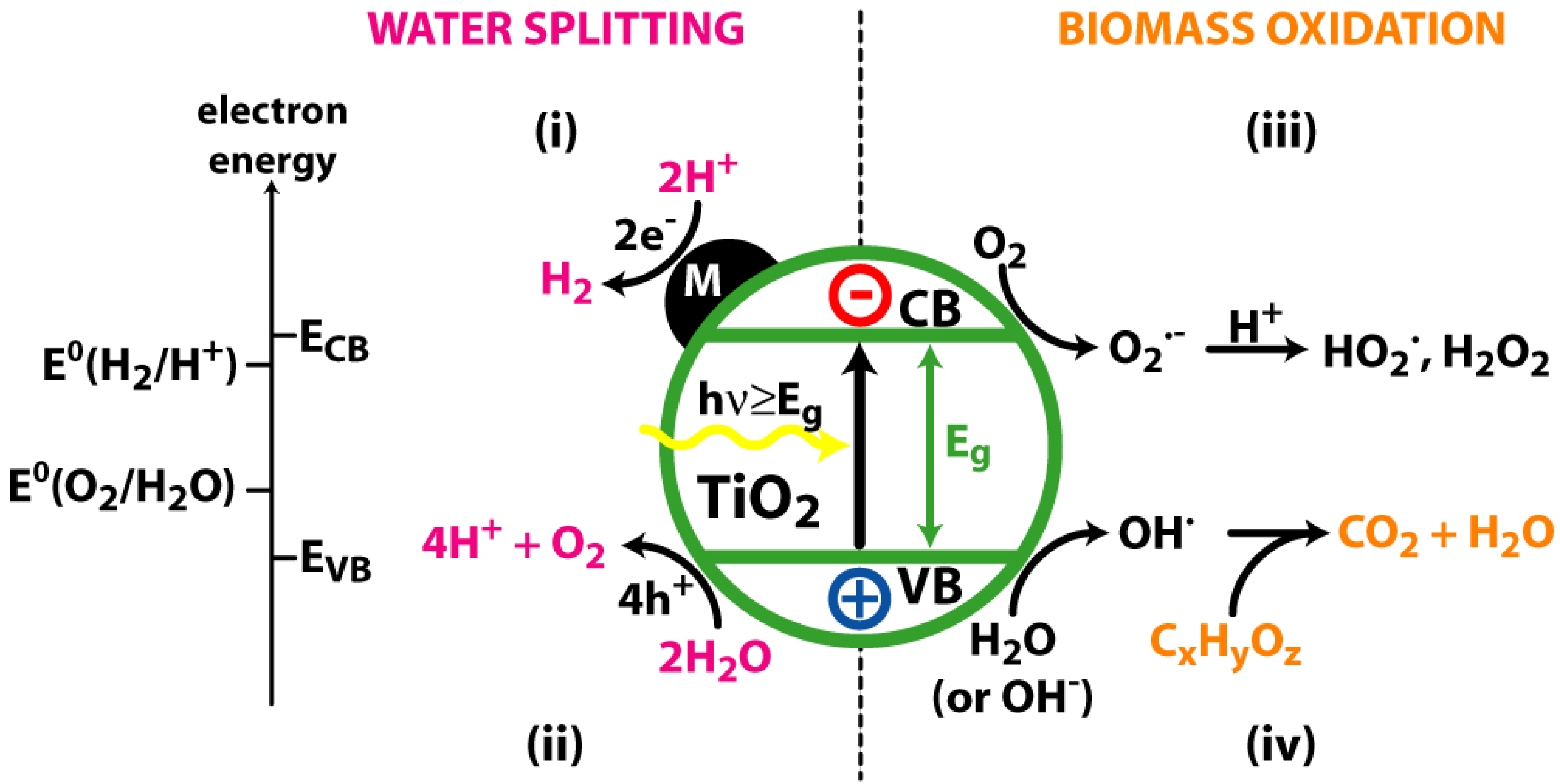
Photocatalytic H_2 production





Fujishima A, Honda K (1972) Nature 238:37
Renewable and Sustainable Energy Reviews **11** (2007) 401-425
Topics in Catalysis 49 (2008) 4-17

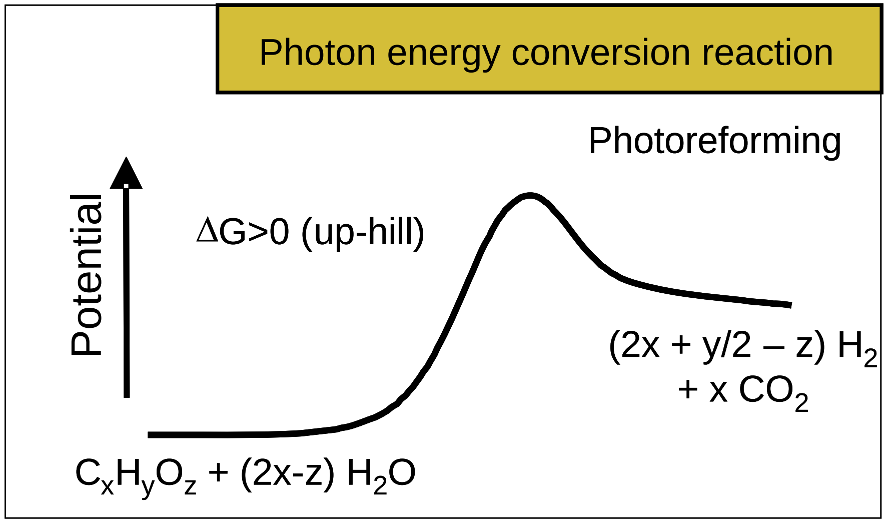
Photocatalytic H_2 production

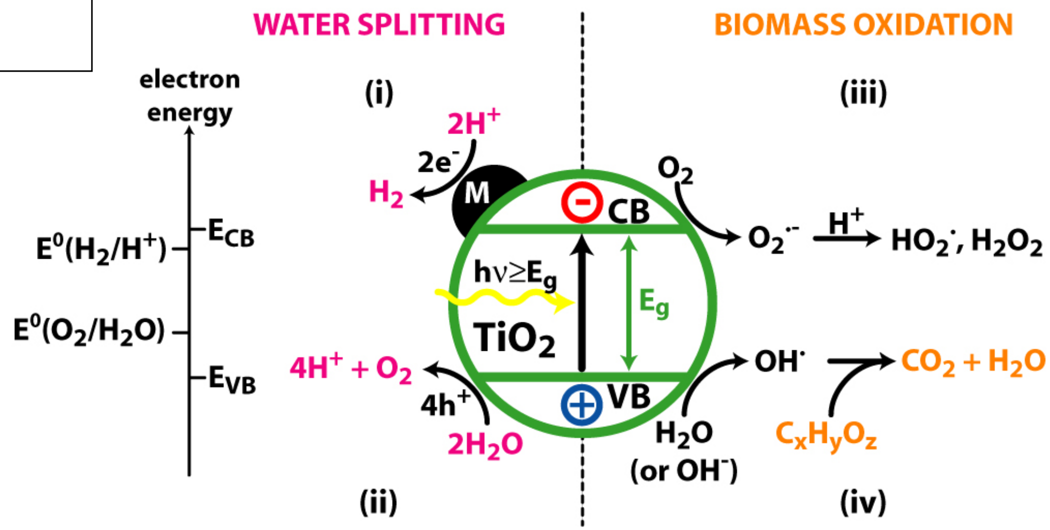


Fujishima A, Honda K (1972) Nature 238:37
Renewable and Sustainable Energy Reviews **11** (2007) 401-425
Topics in Catalysis 49 (2008) 4-17

Photoreforming

$$C_xH_yO_z + (2x - z)\,H_2O \rightarrow x\,CO_2 + (2x + y/2 - z)\,H_2$$





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4. Perspectives

CENMAT

ICCOM

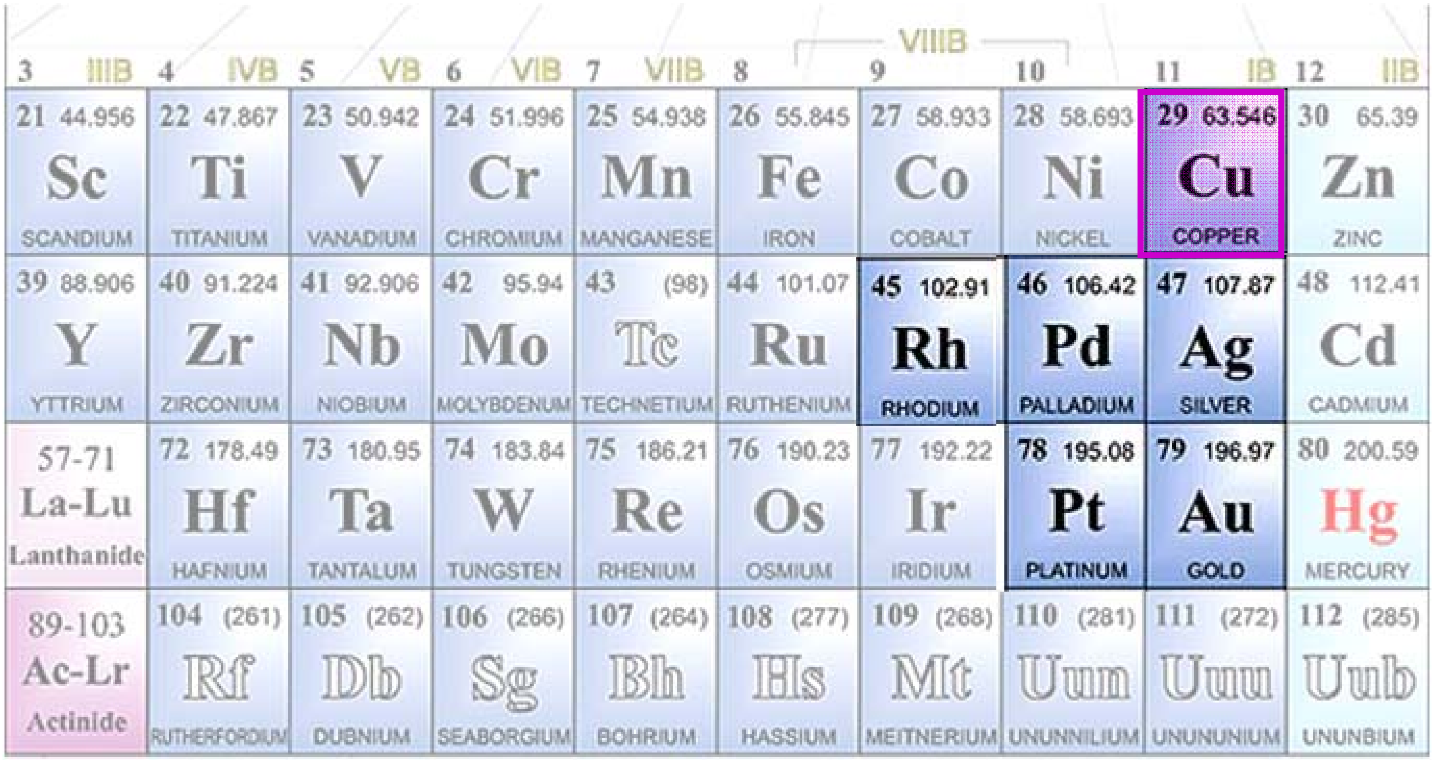
INSTM

Selection of the metal

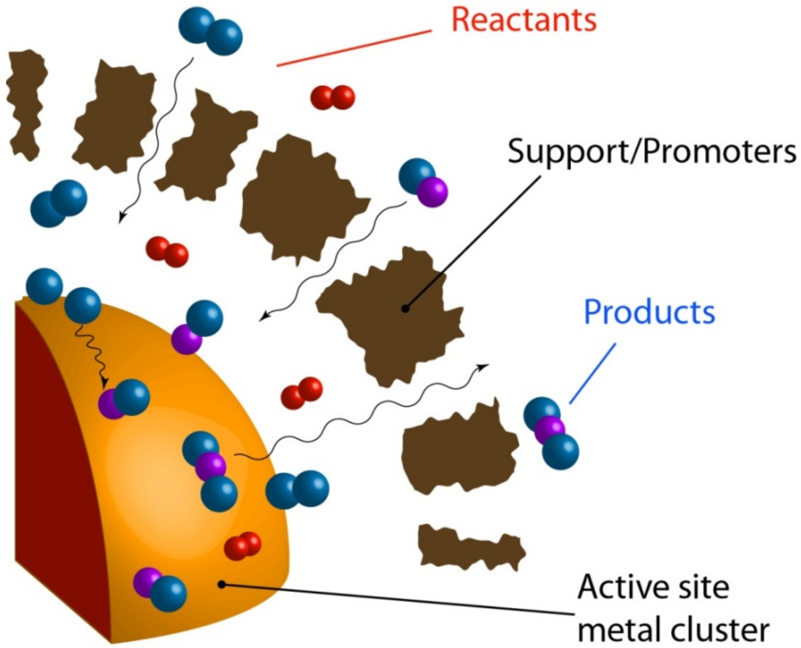
Fundamental conditions: largely available, low cost, non toxic,…

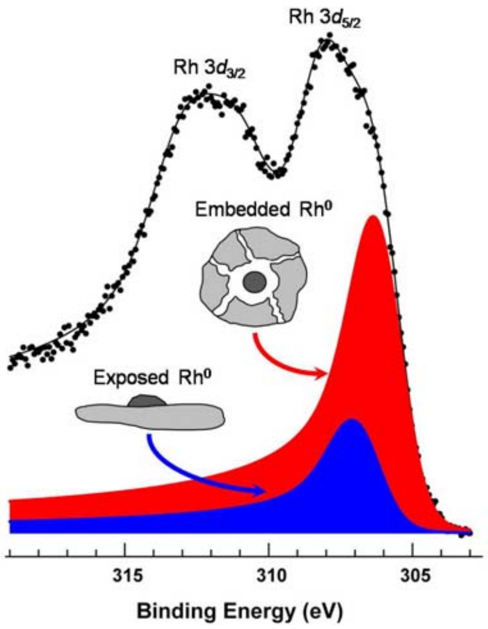
i) M act as electron collector → The Fermi level of the metal is lower than that of TiO_2

ii) Photodeposition of M → Redox potential of M^{n+}/M > energy edge of the conduction band



Photoreforming: the $CuO_x@TiO_2$ system





P. Fornasiero et al., The Journal of Physical Chemistry C 113 (2009), 18069-18074

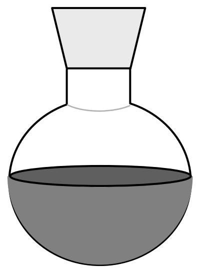
Encapsulation of preformed metal nanoparticles into porous MO_x through different methodologies.

P. Fornasiero et al., ChemSusChem <u>3</u> (2010), 24-42

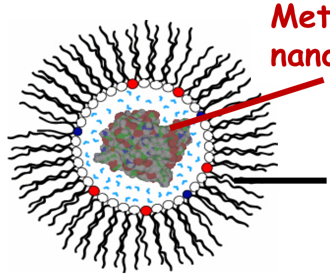
Synthesis: embedding approach

1. Nanoparticles formation:

Microemulsion { Triton X-100, $Cu(NO_3)_2$ } —hydrazine→



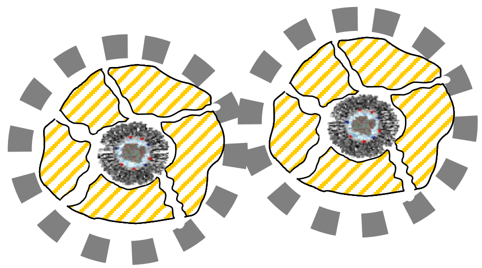
Colloidal Cu dispersion



2. Precipitation of $Ti(OH)_4$

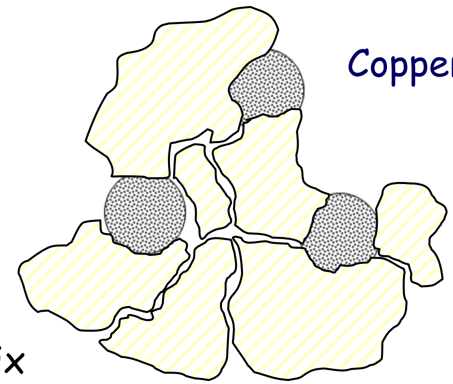
The colloidal Cu dispersion was added to Ti(*i*-PrO)$_4$ in cyclohexane

Aging, filtration and washing



3. Drying and calcination

Calcination 450 °C



Cu(x%)@TiO_2

P. Fornasiero et al. Nanoscience and Nanotechnology Letters 1 (2009), 128-133

Synthesis: CuO_x –TiO_2

1. Microemulsion method

$Ti(i\text{-}PrO)_4$ —(Triton X-100 in cyclohexane / H_2O / hydrazine)→ Precipitation and Aging r.t. → Recovery, Washing, Drying, Calcination 450°C → **TiO_2**

2. Impregnation method

TiO_2 + $Cu(NO_3)_2$ in EtOH → **IMP Cu(x%)/TiO_2**

Stirred 2 h in the dark, dried and calcined 1 h at 450 °C

P. Fornasiero et al., Nanoscience and Nanotechnology Letters 1 (2009), 128-133

Basic characterization of CuO_x@TiO_2 system vs CuO_x –TiO_2 system

		Composition (%)		
	BET Surface area (m^2g)	Anatase	Rutile	Brookite
IMP Cu(2.5%)/TiO_2	64	92	3	5
Cu(2.5)@TiO_2	69	91	6	3

P. Fornasiero et al., Nanoscience and Nanotechnology Letters 1 (2009), 128-133

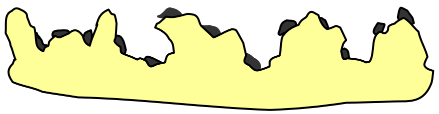
XAFS Characterization

- Cu(II) in the fresh samples

Sample	Shell	N	R (nm)	D_M (nm)
Cu(2.5%)@TiO$_2$ fresh	Cu-O Cu-Cu	3.8 -	0.1962 -	-
Cu(2.5%)@TiO$_2$ irradiated	Cu-O Cu-Cu	4.0 2.2	0.1975 0.2572	0.8

$Cu@TiO_2$

- Partial reduction of Cu after irradiation
- Very small Cu particles



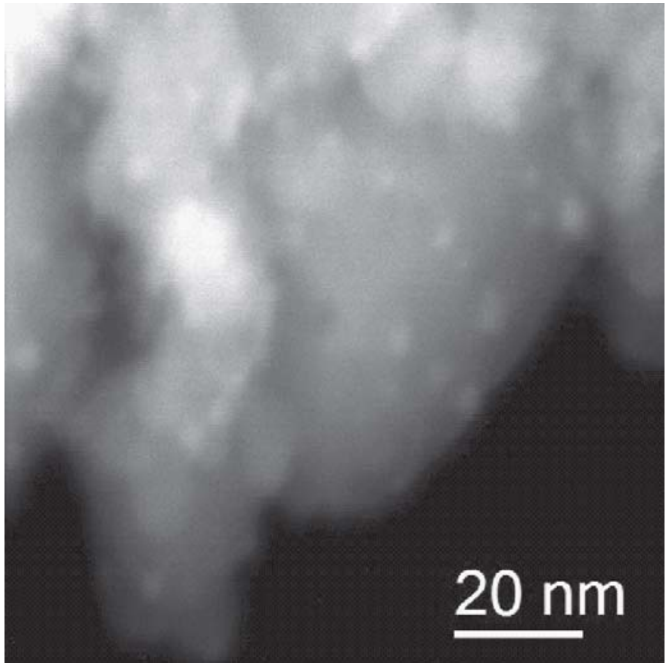
Cu/TiO_2

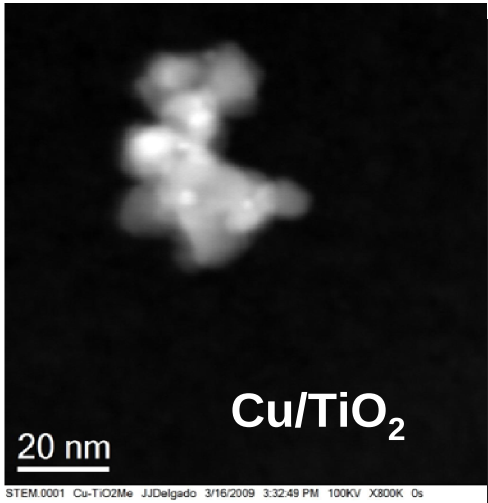
- Very small amount of reduced Cu after irradiation.

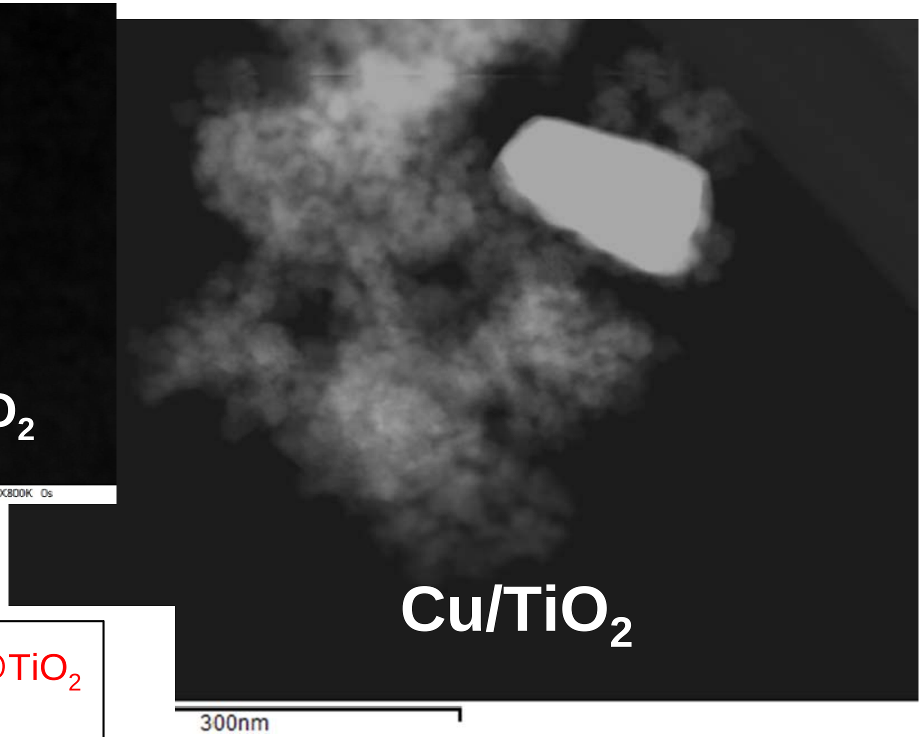
Sample	Shell	N	R (nm)	D_M (nm)
Cu(2.5%)/TiO$_2$ Fresh	Cu-O Cu-Cu	3.5 -	0.1989 -	-
Cu(2.5%)/TiO$_2$ Irradiated	Cu-O Cu-Cu	3.1 -	0.1959 -	-

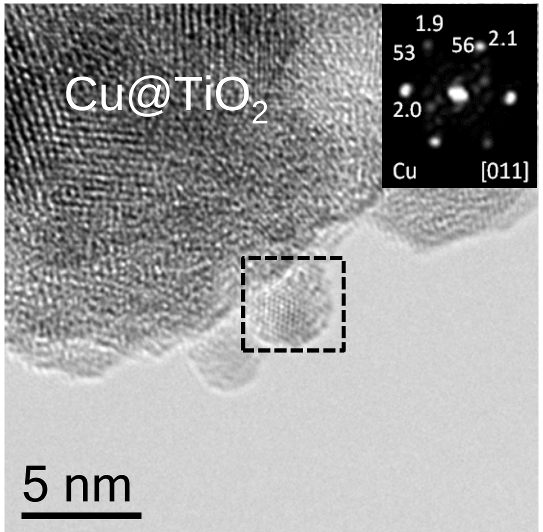
P. Fornasiero et al., J. Phys. Chem. A, 2010, 114 (11) 3916–3925

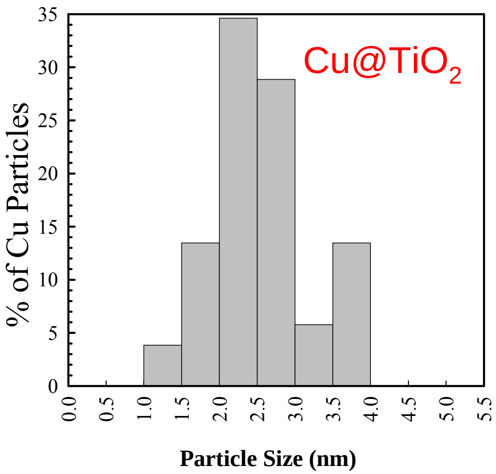
HAADF-STEM Characterization







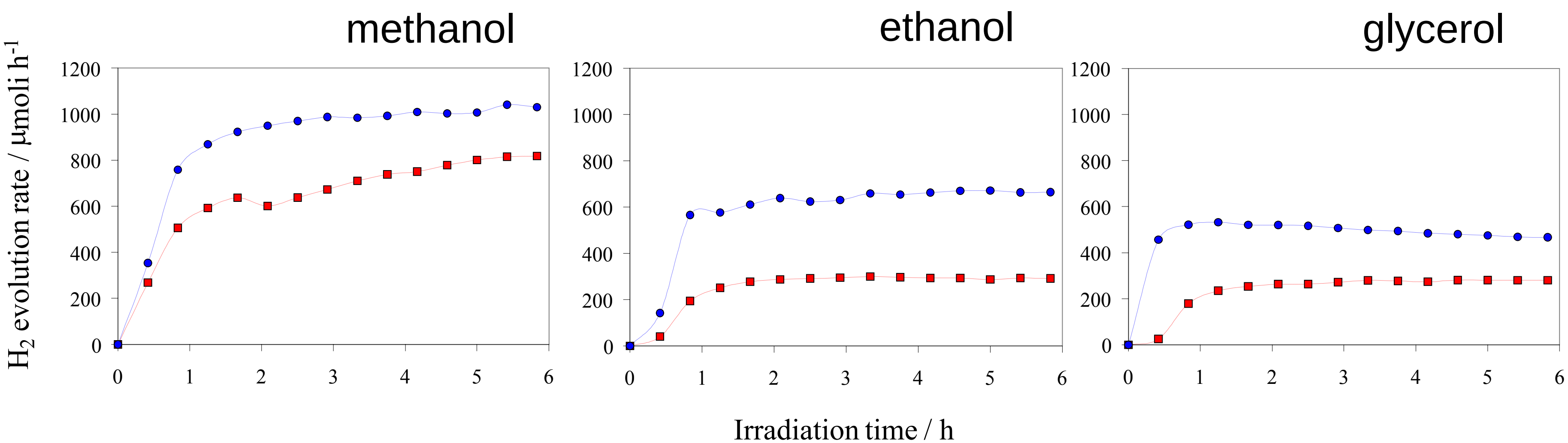


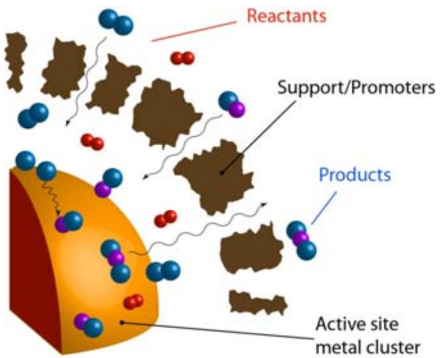


P. Fornasiero et al., J. Phys. Chem. A, 2010, 114 (11) 3916–3925

Photocatalytic hydrogen production

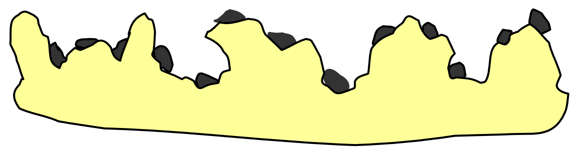
PHOTOCATALYTIC ACTIVITY 2.5% Cu-TiO_2 traditional vs advanced





Advanced

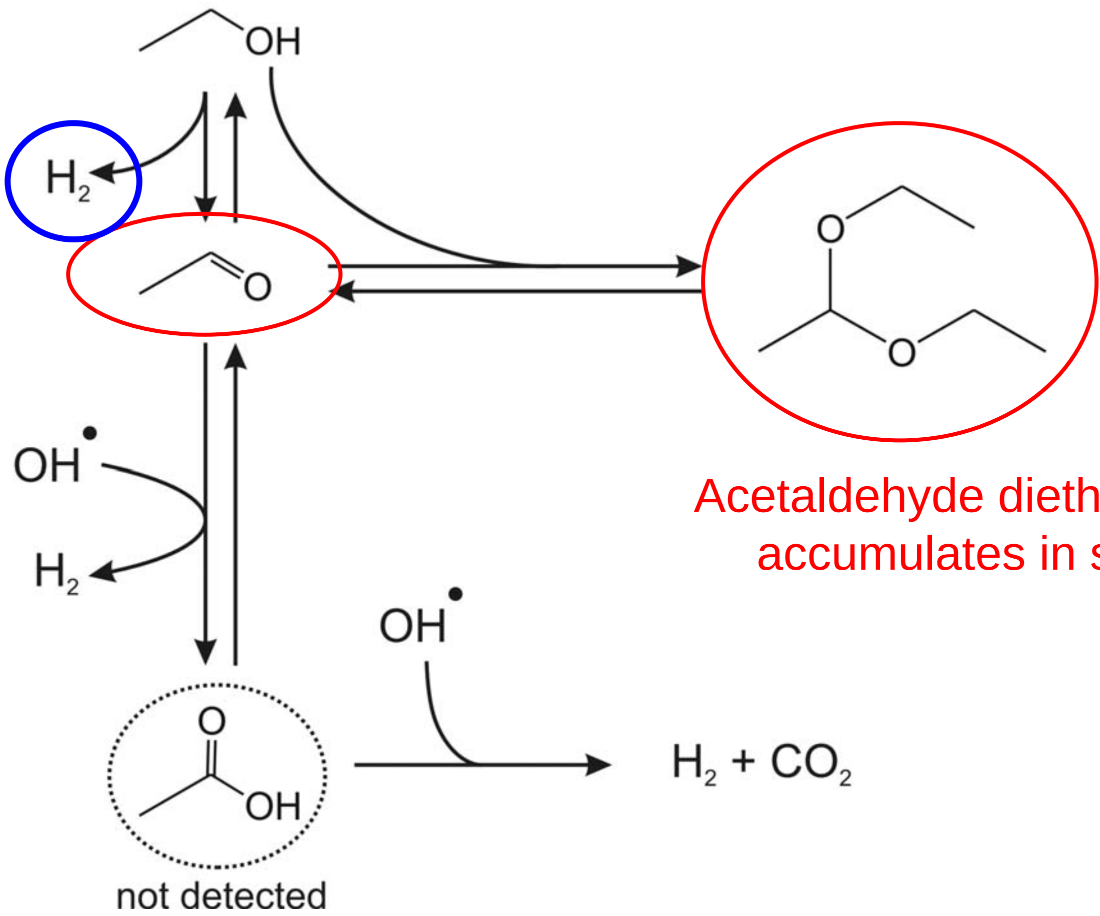
Traditional



P. Fornasiero et al., The Journal of Physical Chemistry A 114 (2010), 3916-3925

CATALYTIC ACTIVITY: H_2 PRODUCTION FROM **ETHANOL**

Possible pathway

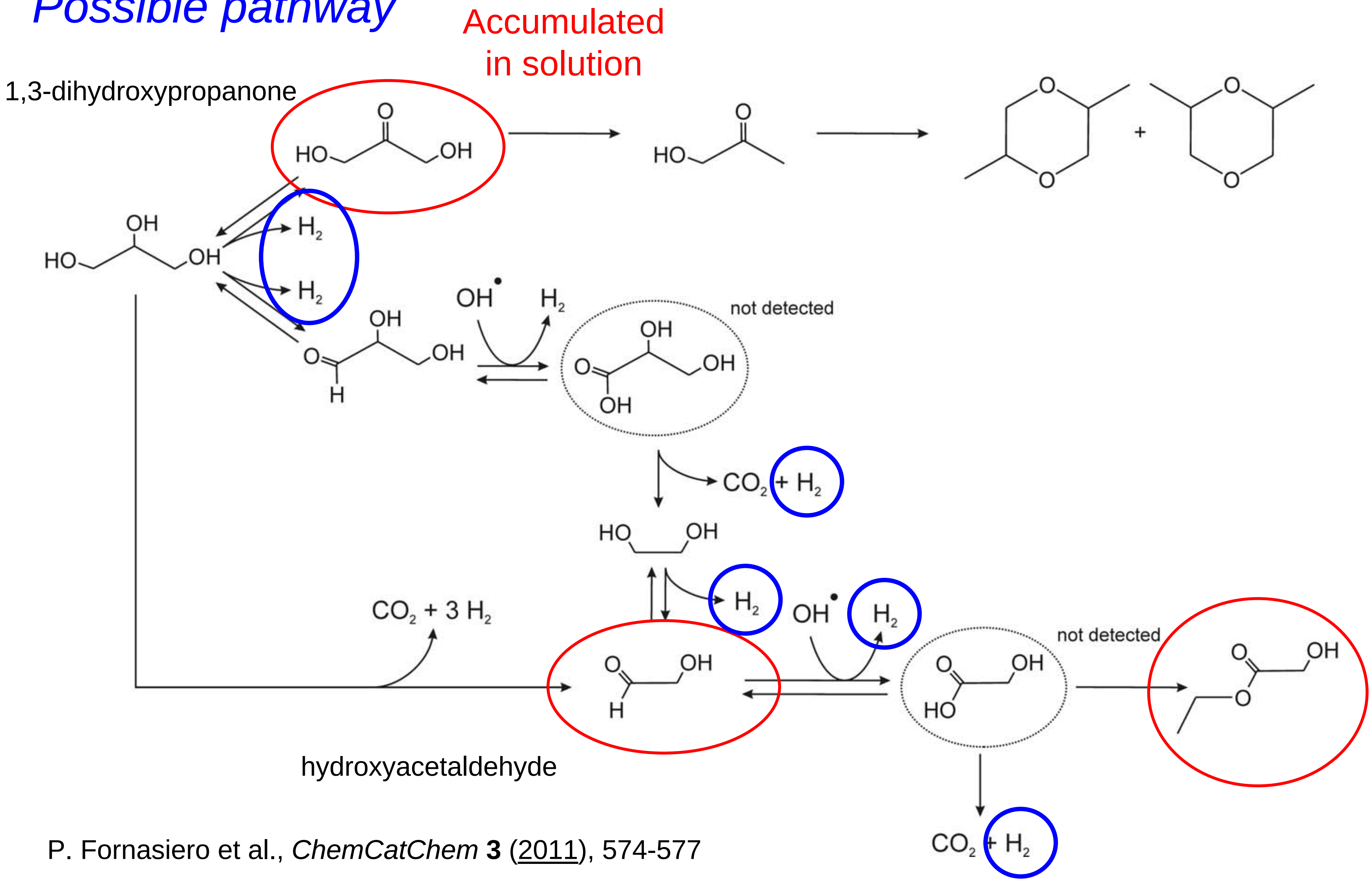


Acetaldehyde diethoxy acetal accumulates in solution

P. Fornasiero et al., *ChemCatChem* **3** (2011), 574-577

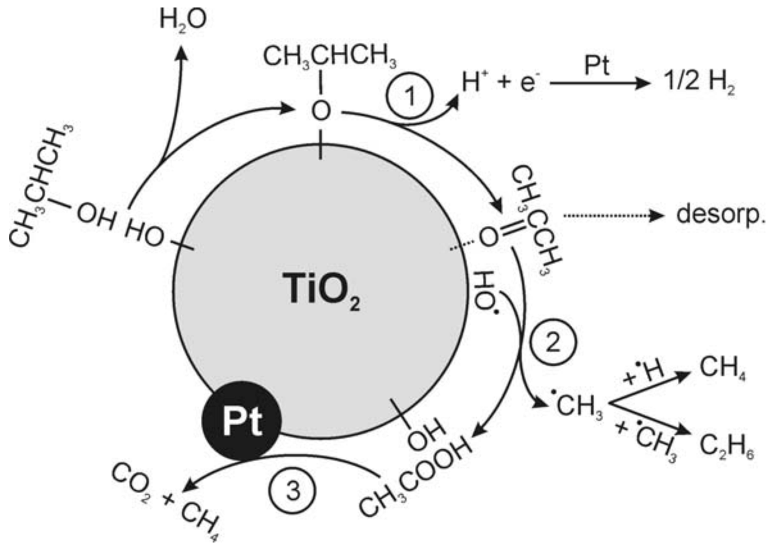
CATALYTIC ACTIVITY: H_2 PRODUCTION FROM GLYCEROL

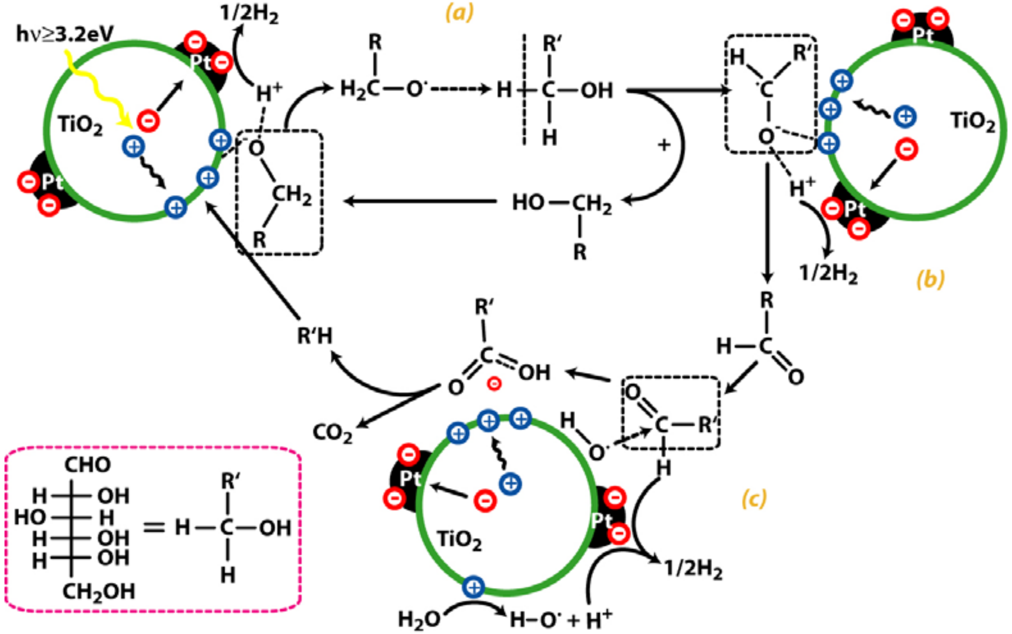
Possible pathway



P. Fornasiero et al., *ChemCatChem* **3** (2011), 574-577

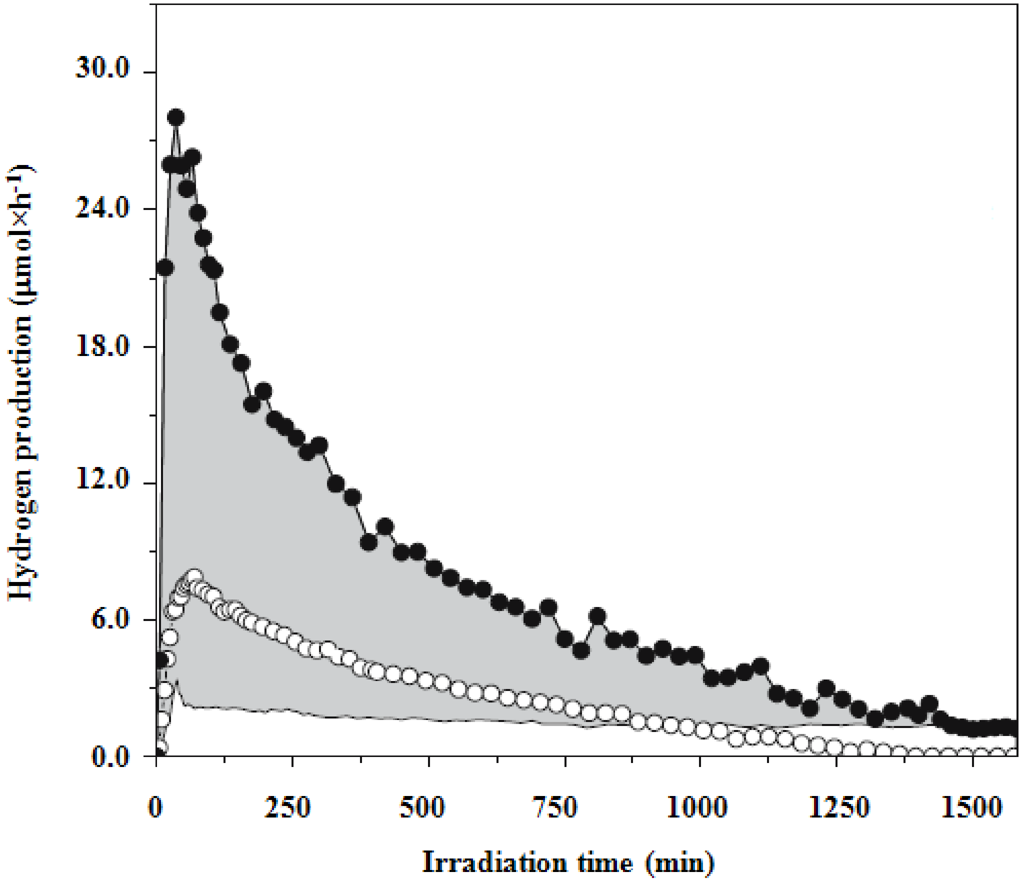
Isopropanol and glucose photoreforming





P. Fornasiero et al., European Journal of Inorganic Chemistry 2011 (2011), 4309-4323

Pt-TiO$_2$ photo-catalysts : stability under glycerol photoreforming



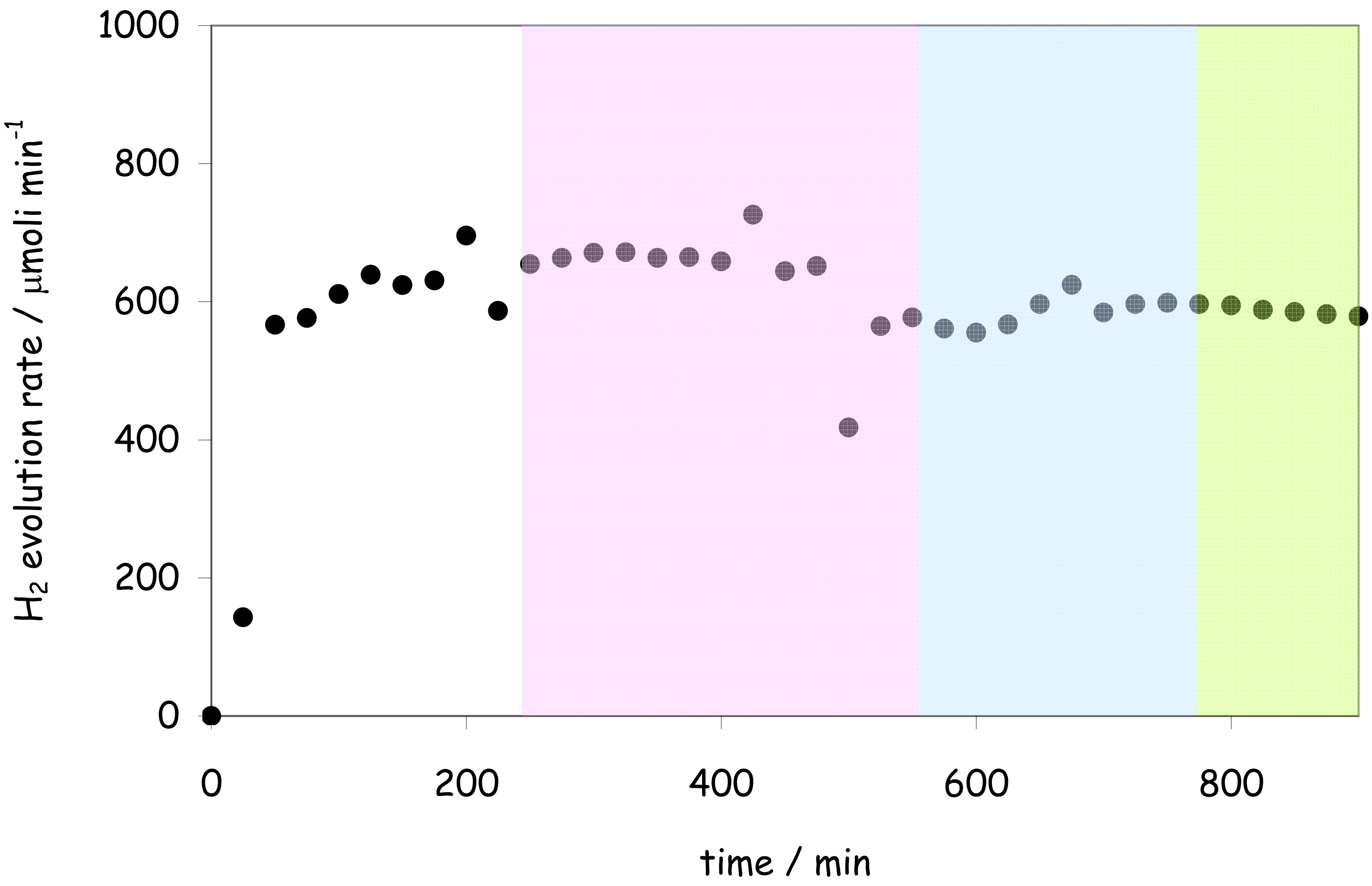
0.368 mM glycerol

D. I. Kondarides, V. M. Daskalaki, A. Patsoura, X. E. Verykios, *Catalysis Letters* **2008,** *122*, 26-32

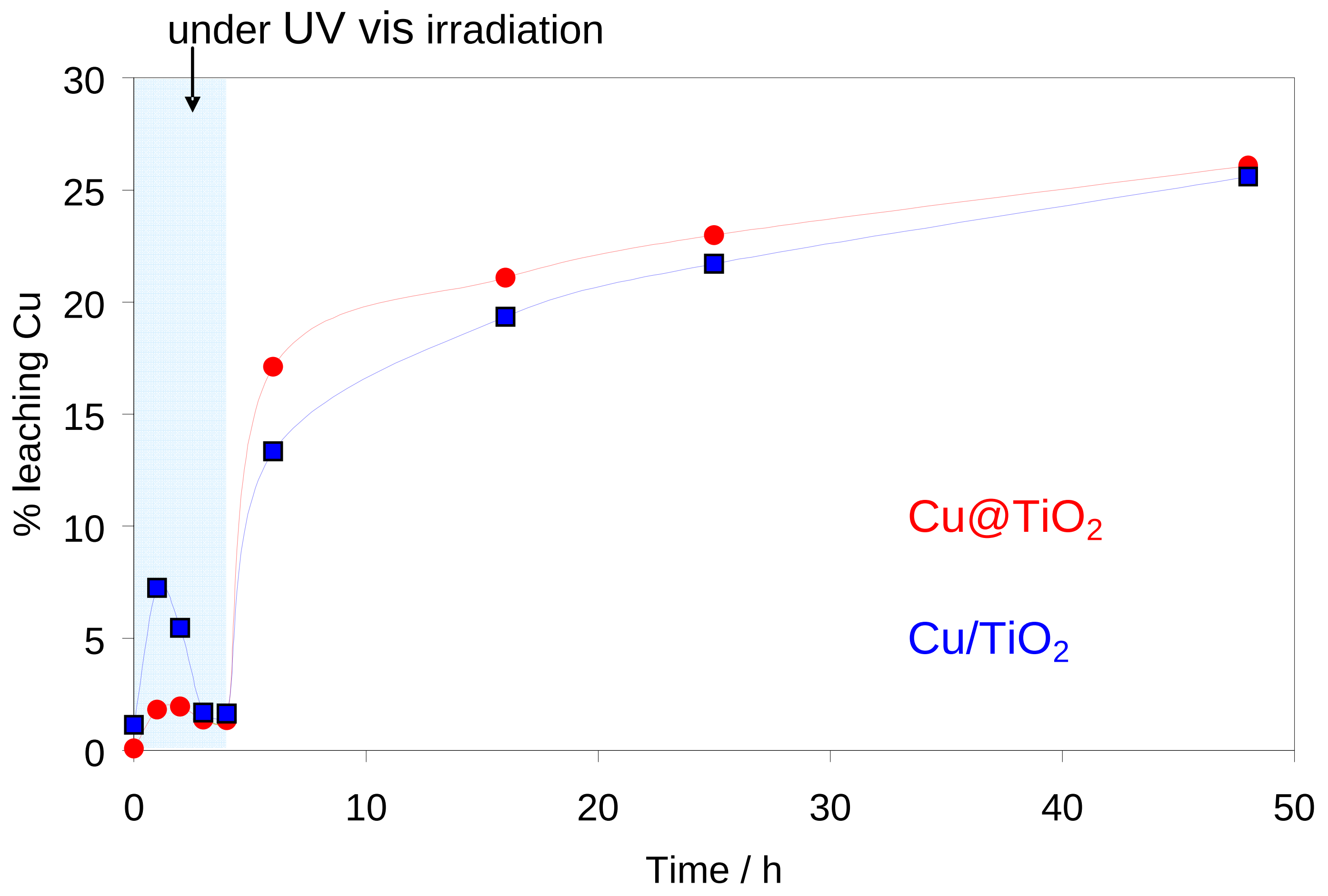
Photocatalytic stability: 2.5% CuO_x@TiO_2

50% water – 50% ethanol

$$CH_3CH_2OH + 3H_2O \xrightarrow{h\nu,\ cat} 6H_2 + 2CO_2$$

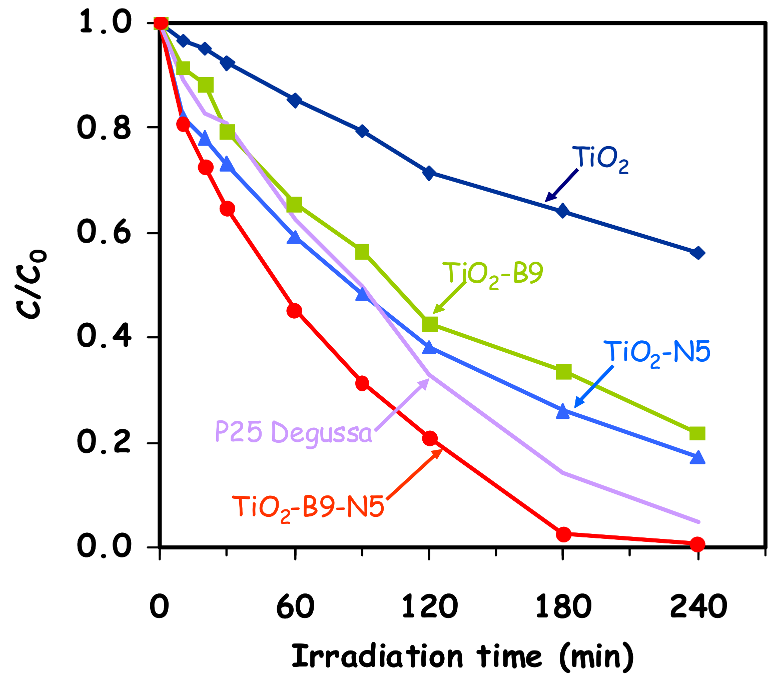


LEACHING Cu



P. Fornasiero et al., The Journal of Physical Chemistry A 114 (2010), 3916-3925

Visible light driven photocatalyst: Pd or CuO_x on B, N co-doped TiO_2



Dyes Degradation

P. Fornasiero, *Chem. Phys.* **339** (2007) 111-123.

Synthesis of the catalyst

Metal photodeposition

Support + metal nitrate → (50% water- 50% methanol; UV-vis irradiation)

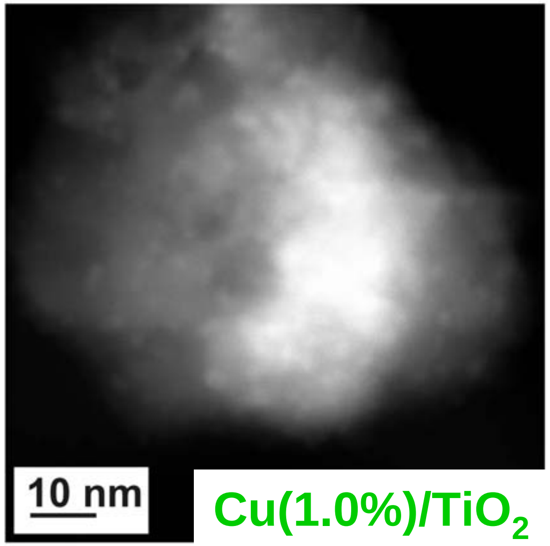
$Pd(0.5\%)/TiO_2$

$Pd(0.5\%)/TiO_2$-B,N

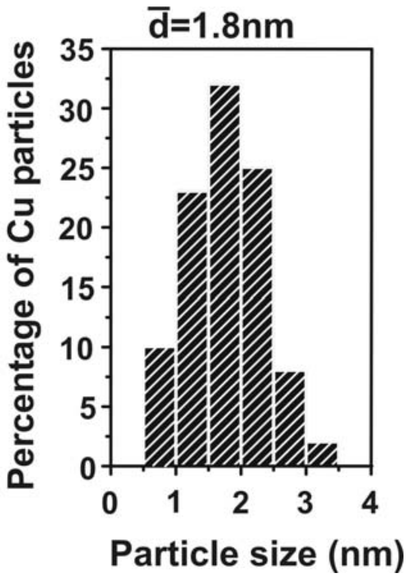
$Cu(1.0\%)/TiO_2$

$Cu(1.0\%)/TiO_2$-B,N

HAADF-STEM



$Cu(1.0\%)/TiO_2$

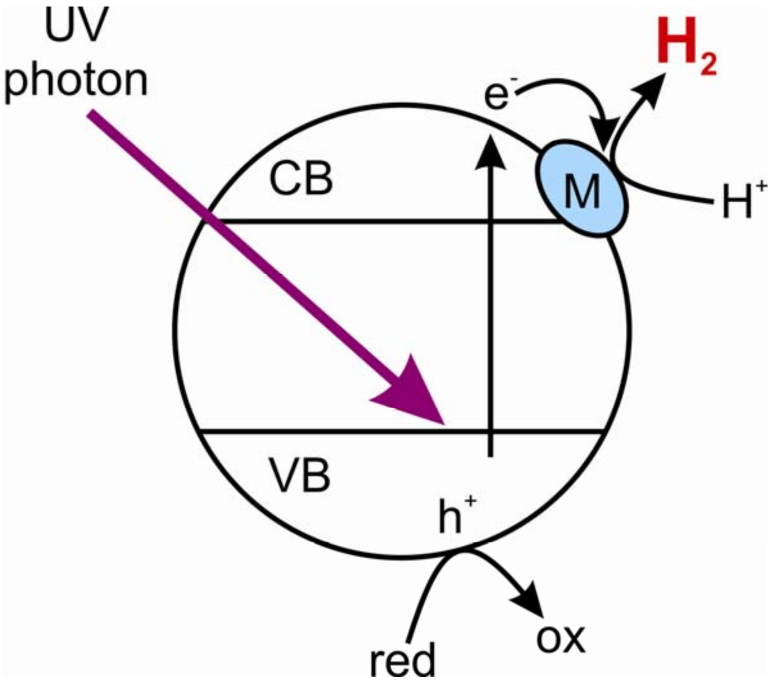


- Highly dispersed metal nanoparticles
- Deposition as M^0 (XANES-EXAFS)
- Texture and phase composition are not affected

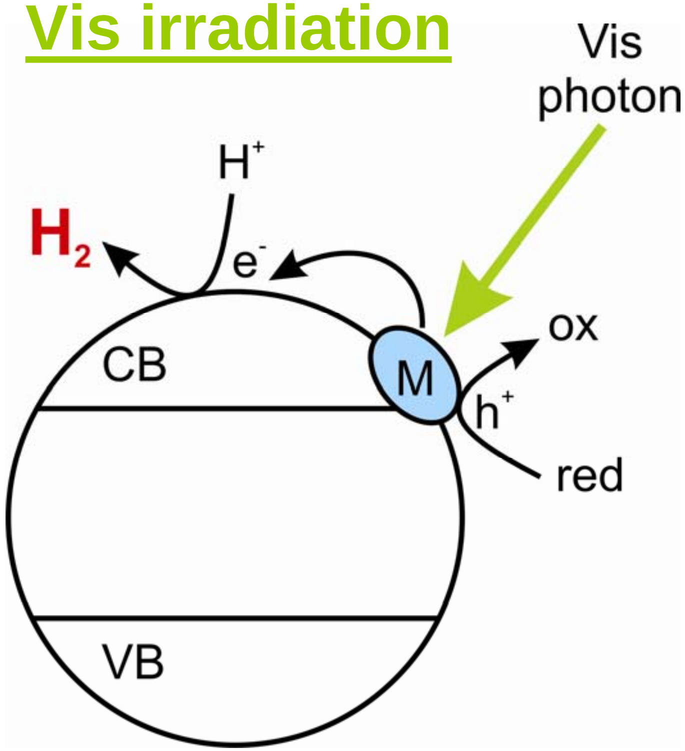
P. Fornasiero, *ChemCatChem* **3** (2011), 574-577

CATALYTIC ACTIVITY: ORIGIN OF Vis ACTIVITY

UV irradiation



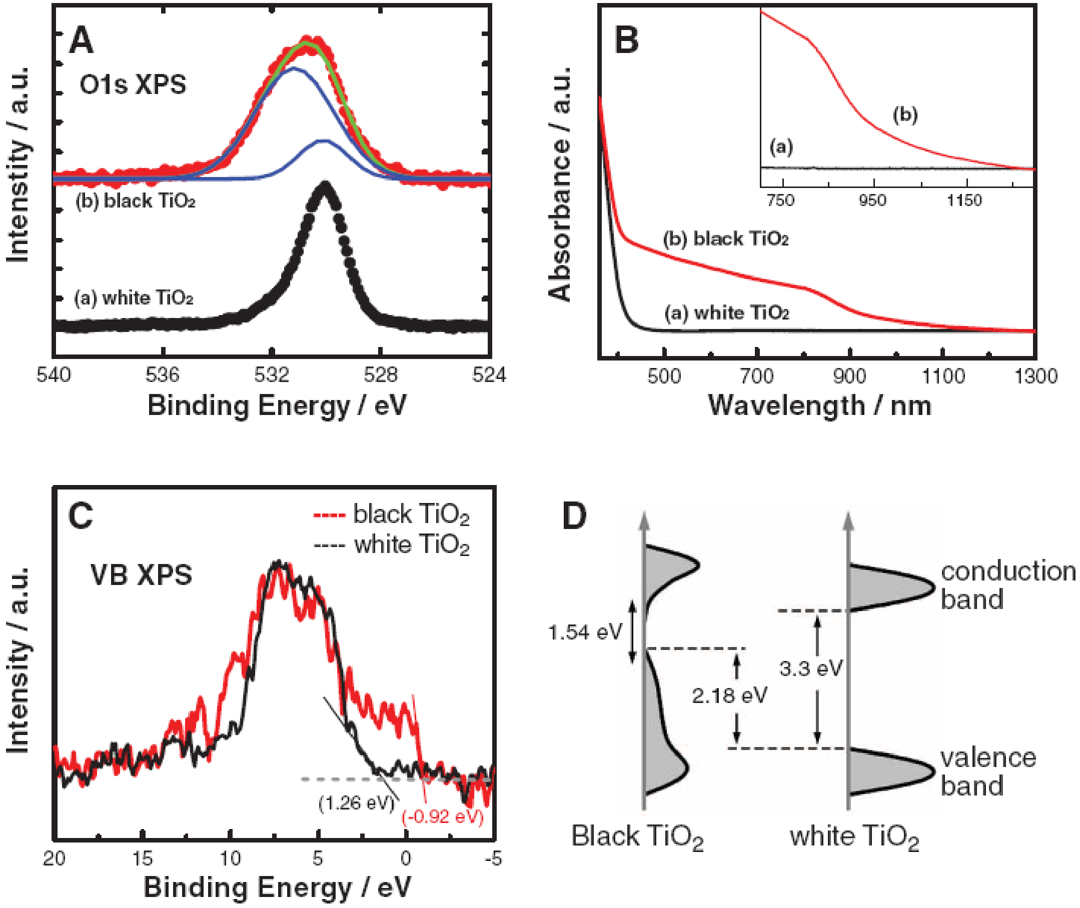
Vis irradiation



As proposed for Au/TiO_2

A. Primo, A. Corma and H. Garcia, *Phys. Chem. Chem. Phys.* **13** (2011), 886-910.

Enhanched photocatalytic activity of hydrogenated black TiO_2



Xiaobo Chen, et al., Science **331**, 746 (2011)

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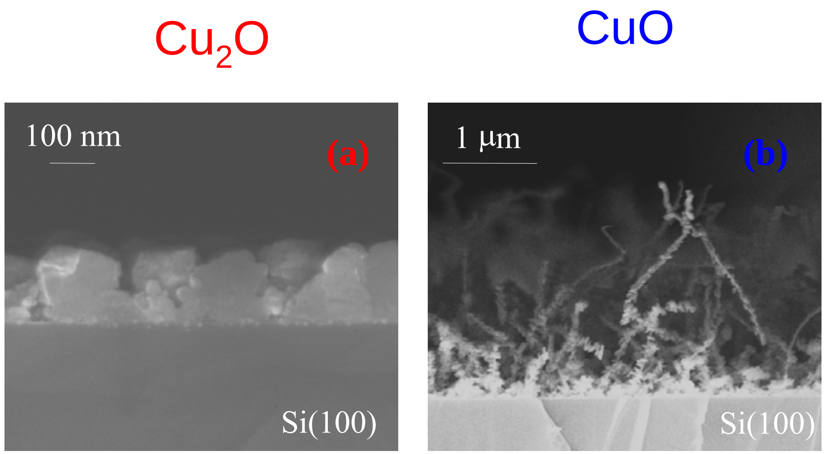
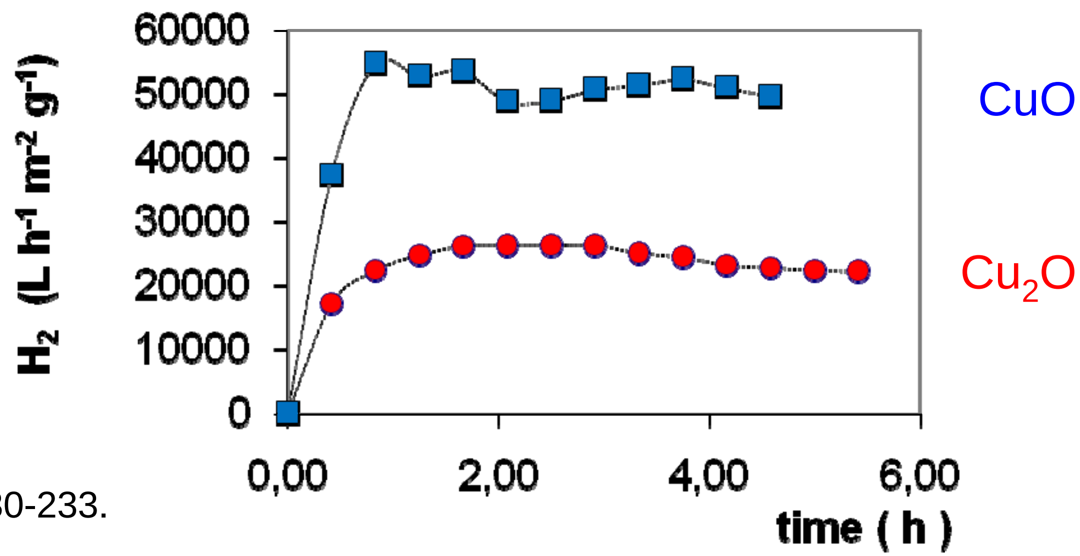
Development of supported CuO_x photo-catalysts

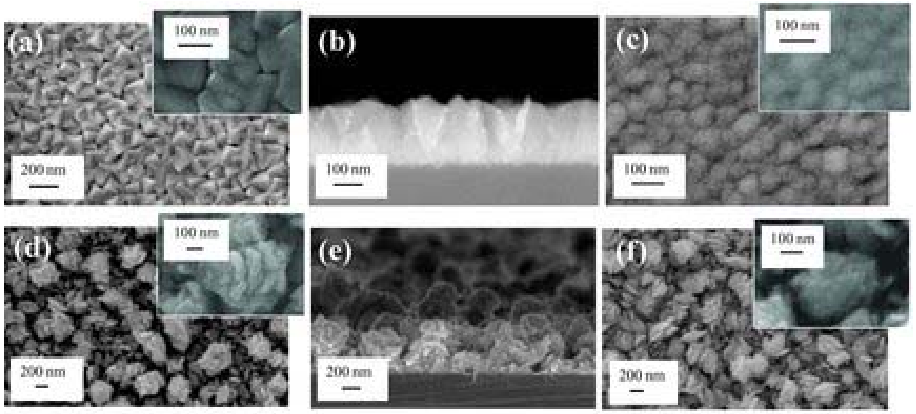


Cu nanustructure and H_2 photo-production from methanol water solution



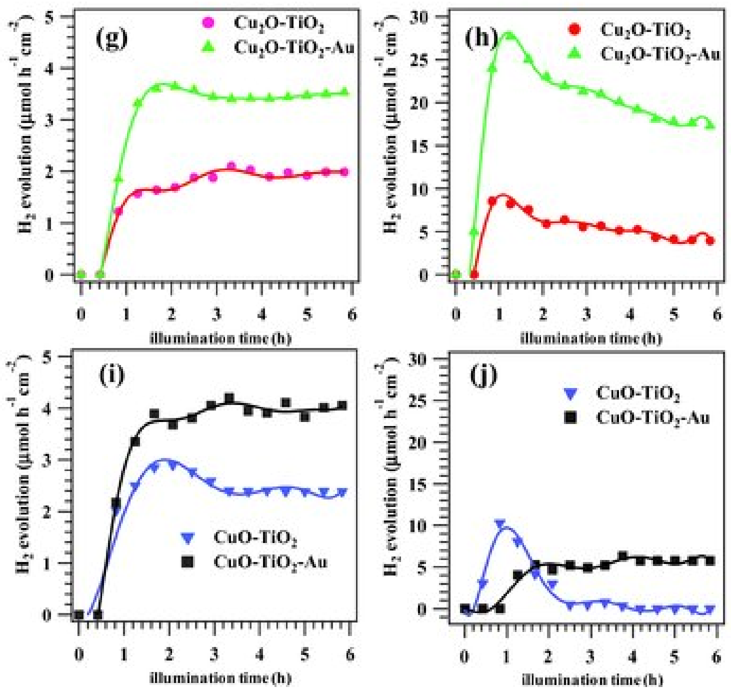
P. Fornasiero et al., ChemSusChem 2 (2009), 230-233.

Bare and Au doped CuO_x/TiO_2 photo-catalysts



VIS

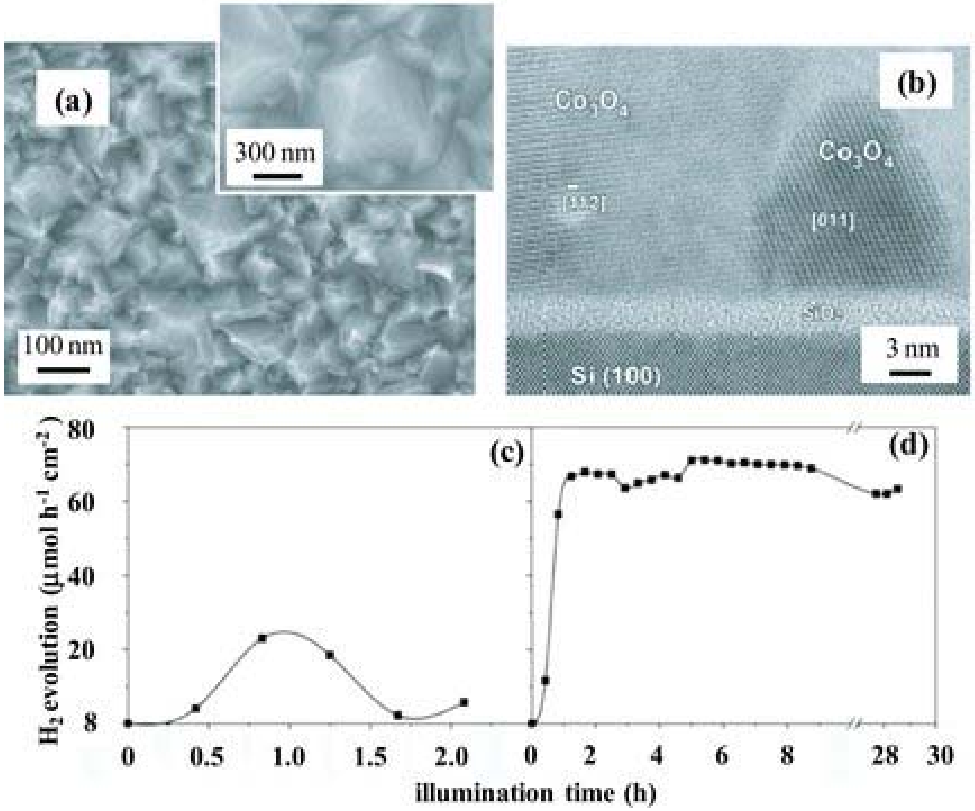
UV



Activity vs stability

P. Fornasiero et al. ,Advanced Functional Materials 21 (2011), 2611-2623

Oxygen assisted H_2 production over Co_3O_4 photocatalysts



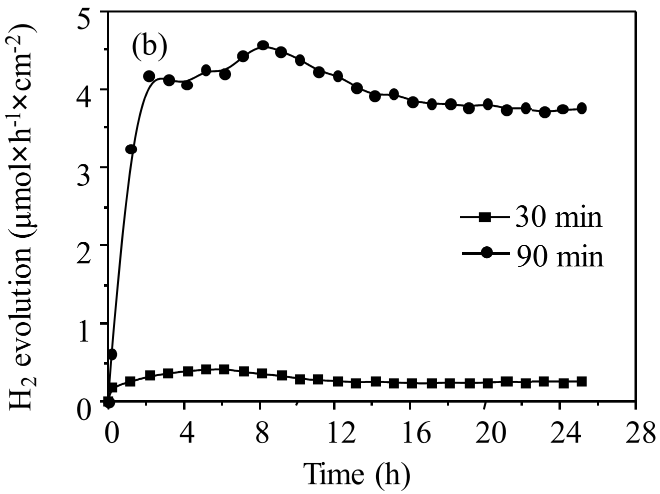
Oxygen free

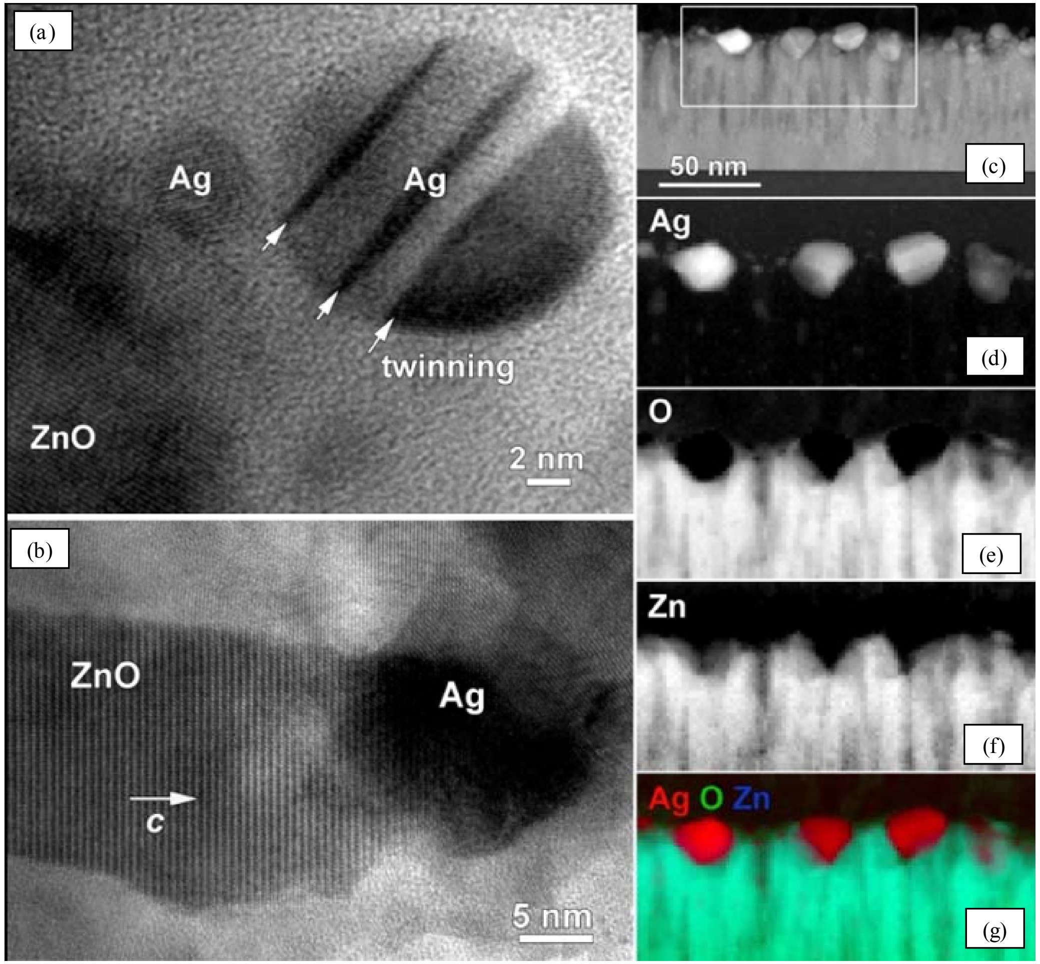
Oxygen assisted

P. Fornasiero et al., Chem. Vap. Deposition 2010, 16, 296

Ag/ZnO nanocomposite photocatalysts

H_2O/CH_3OH solutions





P. Fornasiero et al., International Journal of Hydrogen Energy (2011), in press, doi:10.1016/j.ijhydene.2011.09.045

Perspectives

Photocatalytic reforming of renewable oxygenates to produce hydrogen is an attractive research topic.

In order to transform it into a technological process, we must:

- Increase photocatalytic efficiency
- Increase activity under visible light irradiation
- Increase stability
- Explore its potential use in water-water treatments
- Explore simultaneous hydrogen production and valorisation of the partially oxidized byproducts

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Our web site: *www.dsch.units.it/~fornasiero/index.htm*

Dr. D. Barreca, Dr. A. Gasparotto, Prof. E. Tondello University of Padova and CNR
Dr. V. Dal Santo, Dr. R. Psaro, CNR - Milano

- University of Trieste
- INSTM Consortium
- ICCOM-CNR
- Fondazione CRTrieste
- Fondo Regione FVG

Thank you for your attention