La production d'hydrogène décarboné par voie photo(electro)catalytique solaire

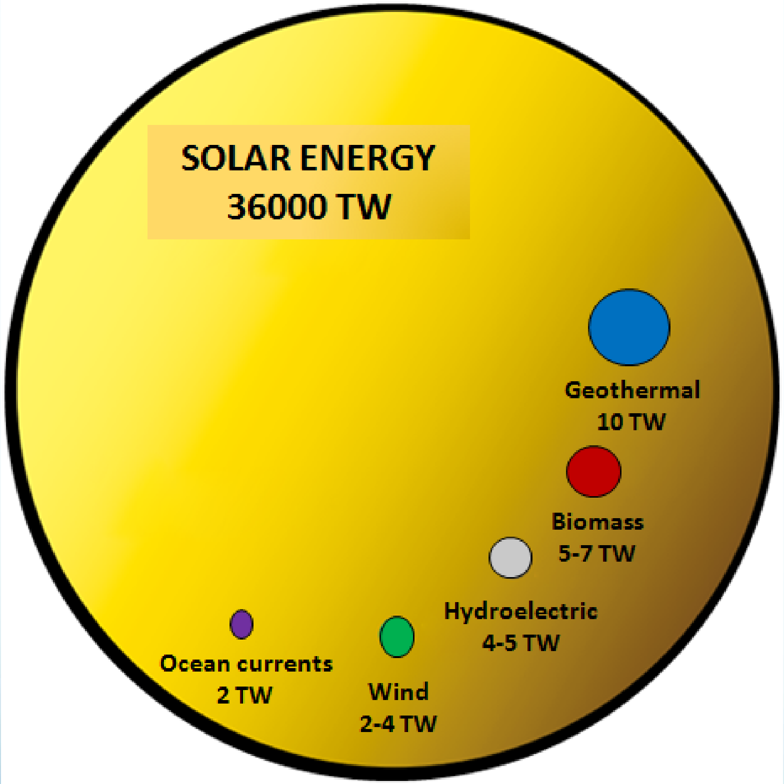
Institute of Chemistry and Processes for Energy, Environment and Health (ICPEES)

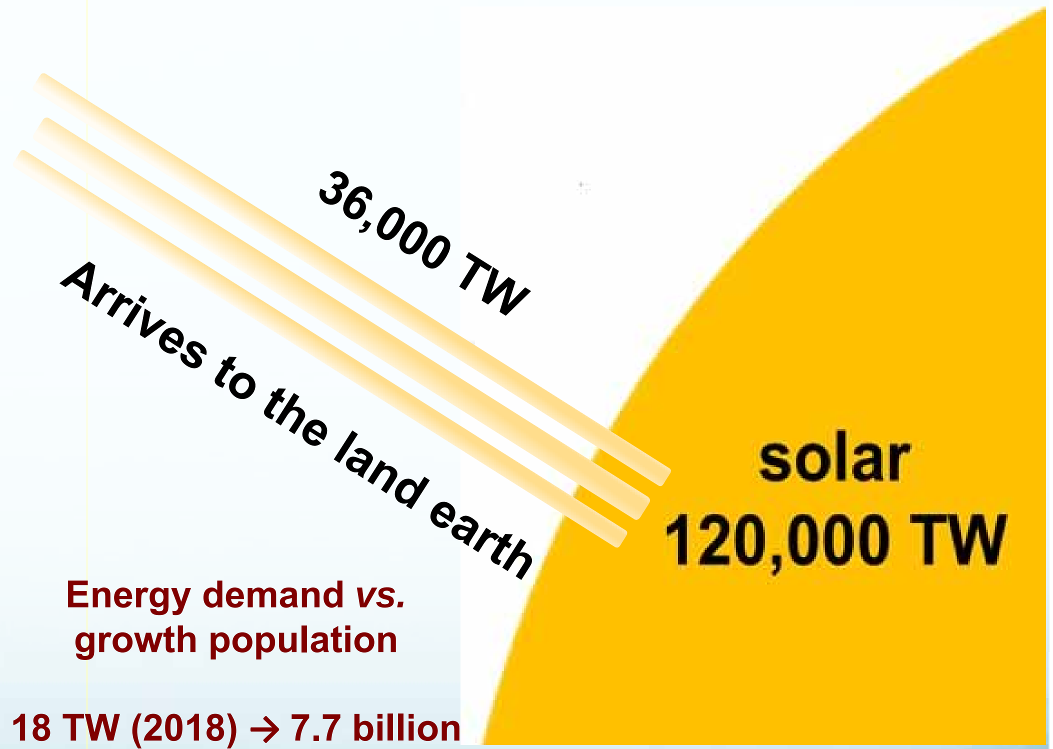
Photocatalysis, Photoconversion and Green Chemical Processes team

SUNRISE
European Consortium

The global Energy challenge

➢ **Consider renewable energy technologies as complementary ones**





➢ **Solar influx during few hours might cover our yearly consumption**

Renewable (solar) energy storage

Solar energy is the most abundant renewable energy BUT it is intermittent and not homogeneously distributed

➢ **Need for solar energy storage**

➢ **Solar energy storage into chemical bonds to be further used on demand: Solar Fuels**

H_2 production from water

CO_2 recycling for production of liquid fuels

Hydrogen: 140 $MJ.kg^{-1}$
Natural gas: 55 $MJ.kg^{-1}$
Oil: 45 I
Li-ion b 1

Fossil sources

- Vapo-reforming
- Partial oxidation

Biomass

- Thermochemical
- Catalytic

Water

- Thermochemistry
- Electrolysis
- **Photoelectrochemistry**
- **Photocatalysis**

What kind of renewable energy ?

Land area required for different « renewable energies sources »

Europe beyond 2050:
700 million people - 2 TW power

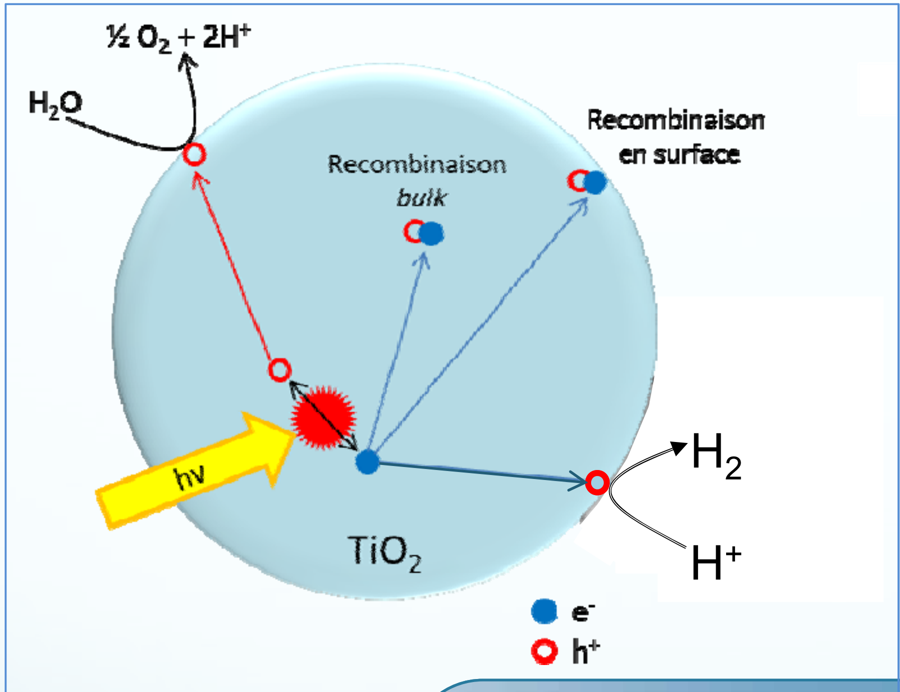
Efficiency of solar conversion	Surface per capita	Total area needed	
100 %	30 m²	0.3 %	
10 %	300 m²	3 %	**Artificial Photosynthesis**
1 %	3000 m²	30 %	
0.1 %	30000 m²	300 %	**Biomass**

Average power consumption per capita ~6kW for European citizens

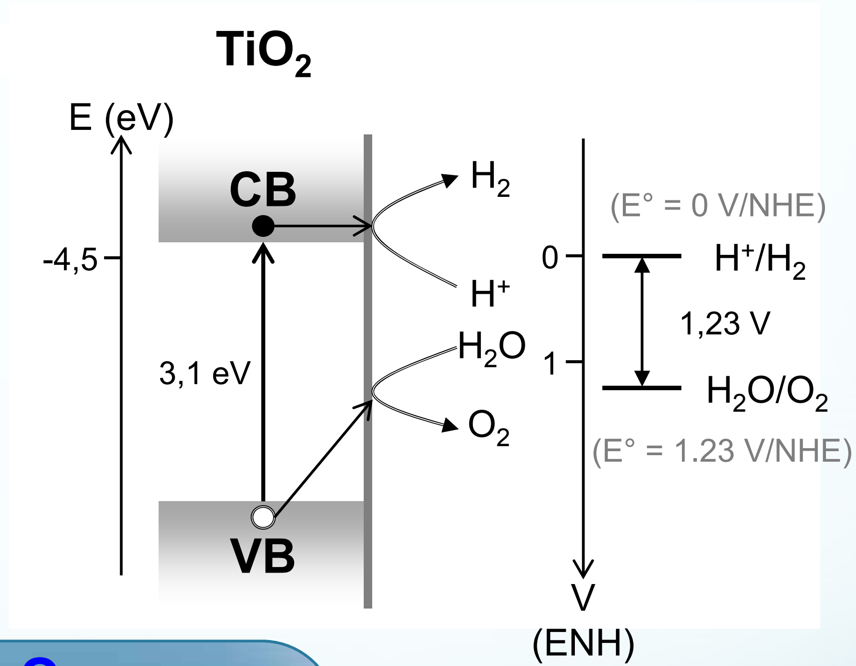
Assuming that 50% comes from solar fuels
Insolation average
~ 100 W/m²

Principle of water-splitting

Activation



Energetically



$H_2O \rightarrow H_2 + ½ O_2$

Redox reactions

Redox couples **H_2/H_2O et O_2/H_2O**

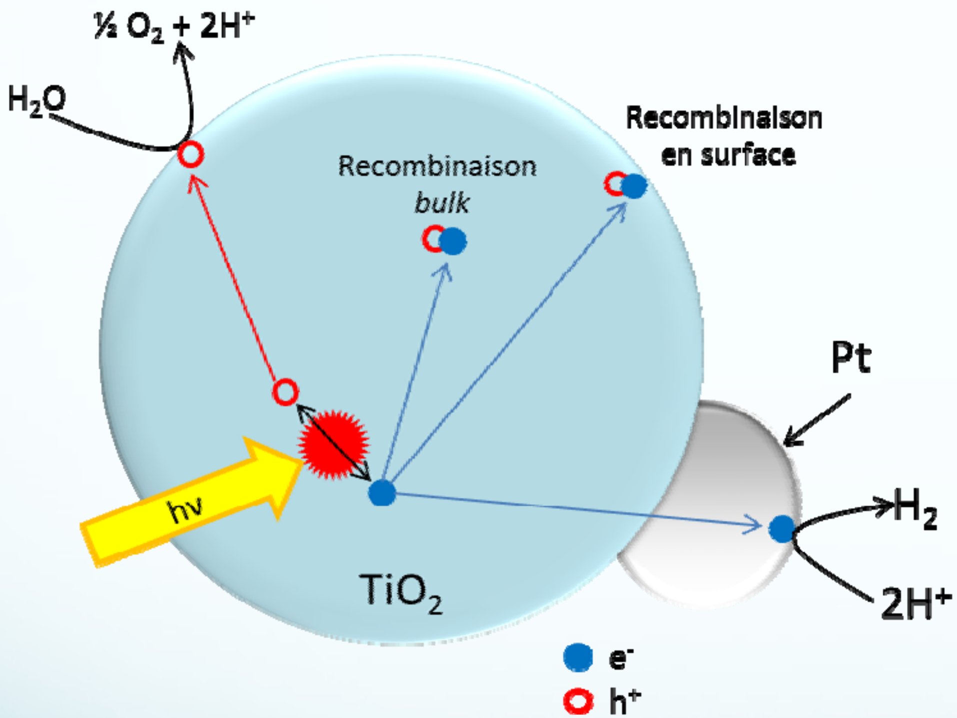
$$2H_2O \rightleftharpoons 2H_2 + O_2 \quad E = 1,23\ V$$

$2H^+ + 2e^- \rightarrow$ **H_2** (0.0 V)

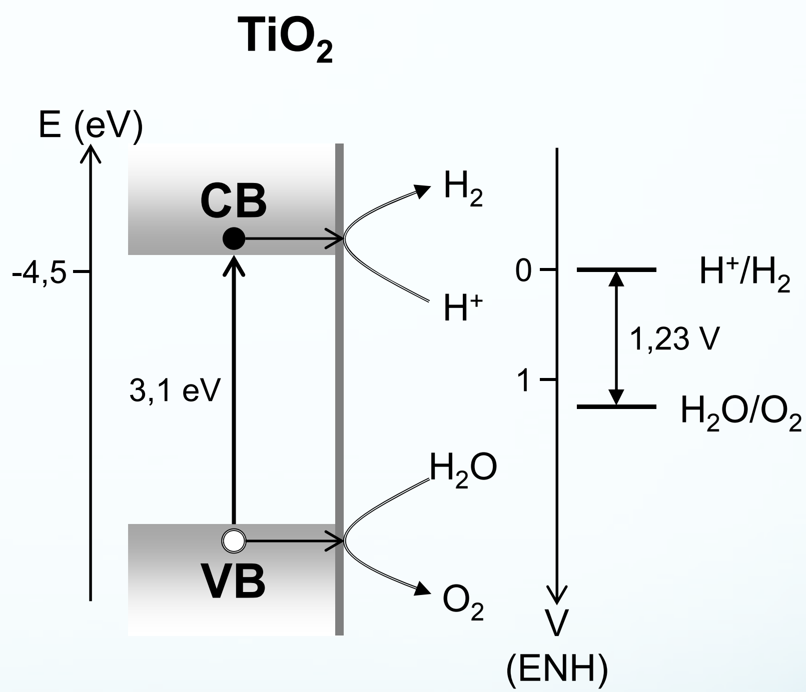
$H_2O + 2h^+ \rightarrow ½$ **O_2** $+ 2H^+$ (1.23 V)

Principle of water-splitting

Activation



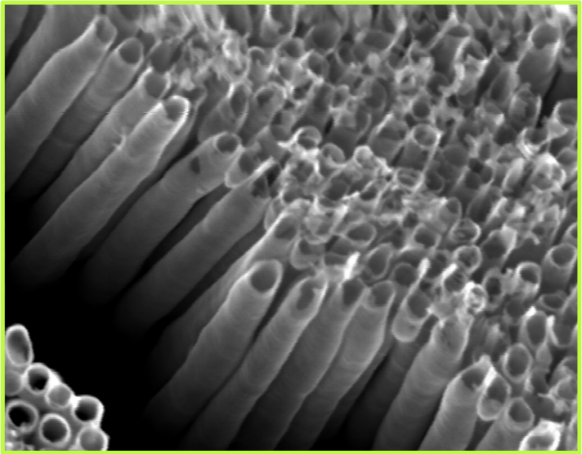
Energetically



Main limitations

- Using TiO_2, difficut to perform reduction step : Addition of metallic co-catalyst
- Back reaction: thermodynamically favoured
- Charges recombination
- TiO_2 anatase: Band-gap = 3.2 eV, requires UV-A activation

Photoelectrochemical appro

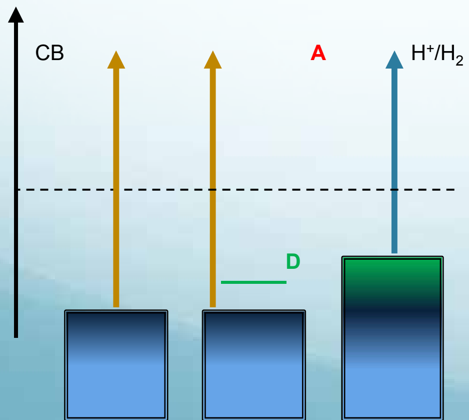


Photoanode

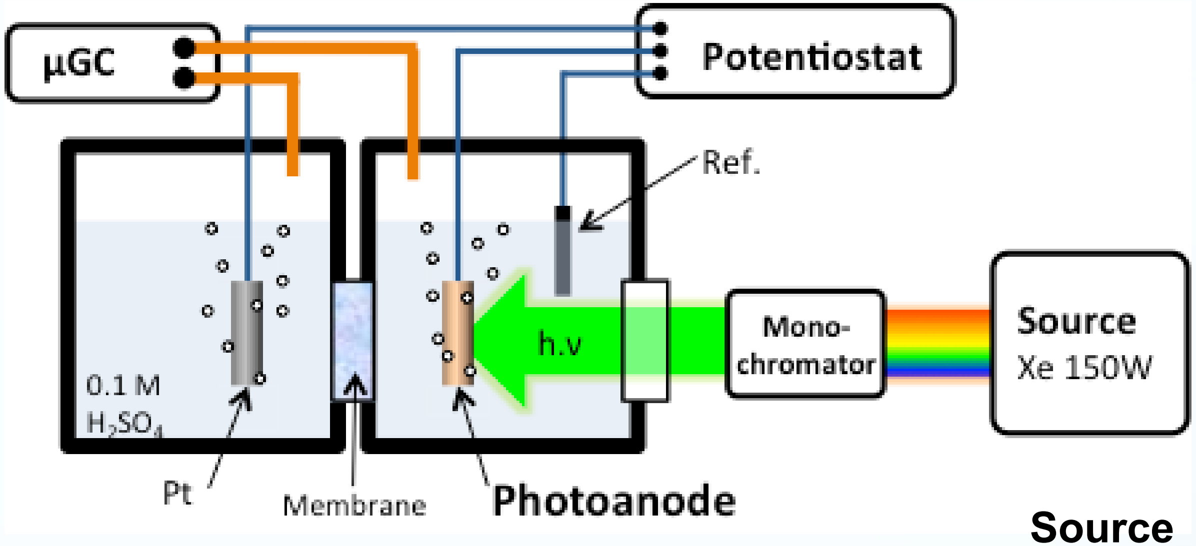
Modified aligned TiO_2 nanotubes

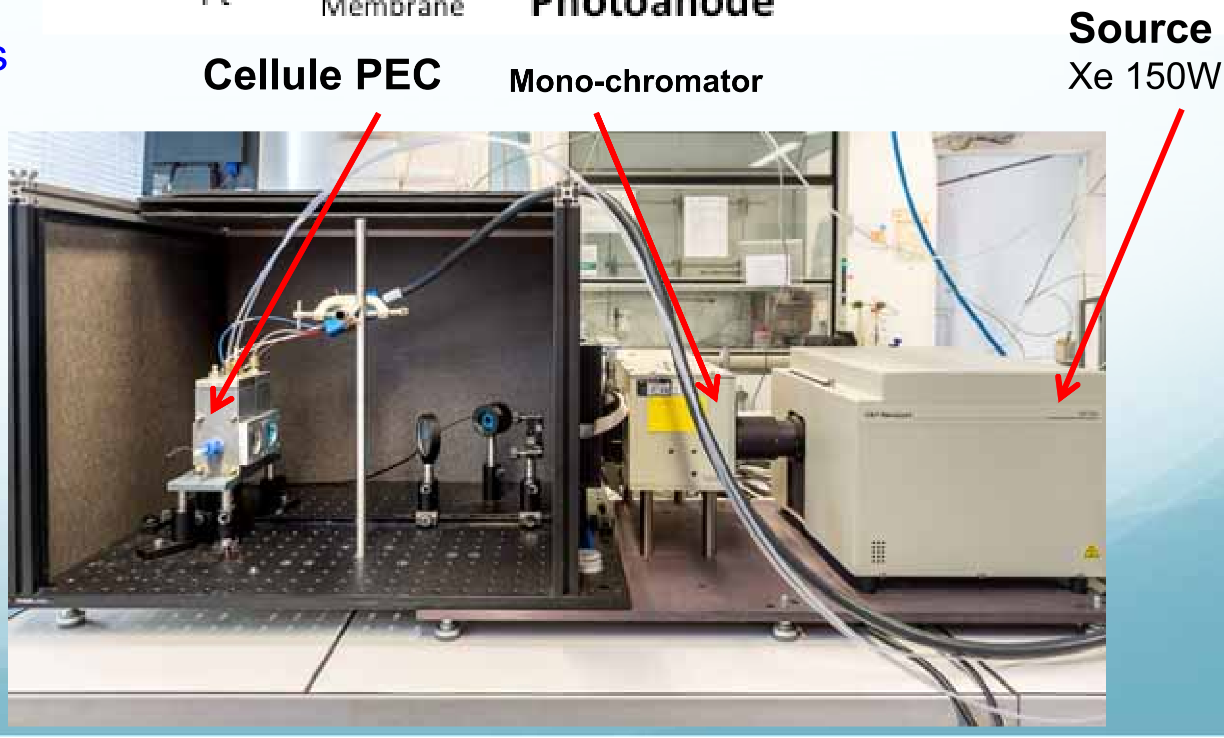
$$Ti^{4+}_{(1-x)}\ M^{(4+n)+}_{x}\ O^{2-}_{(2-\frac{n}{p}x)}\ A^{(2+p)+}_{\frac{n}{p}x}$$

TiO_2 | N doping | Co-Alloying

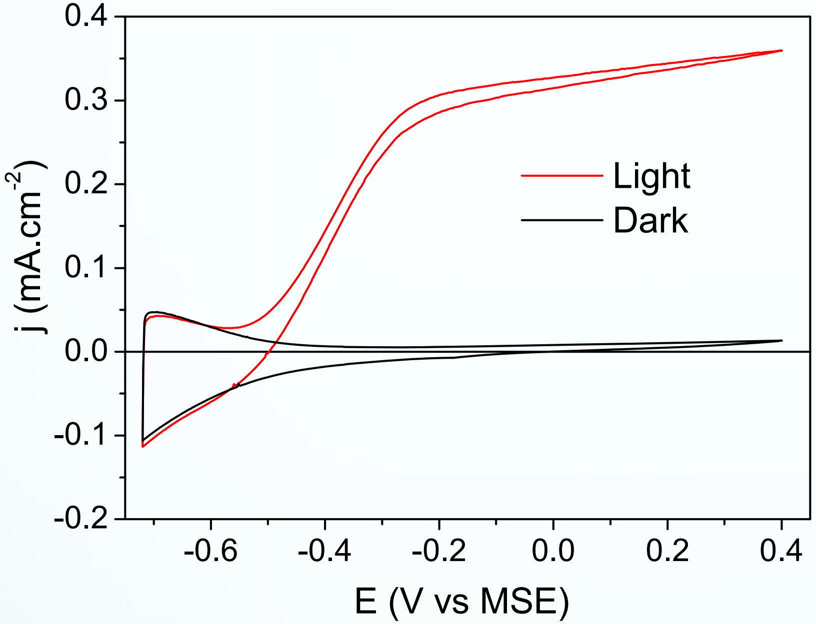


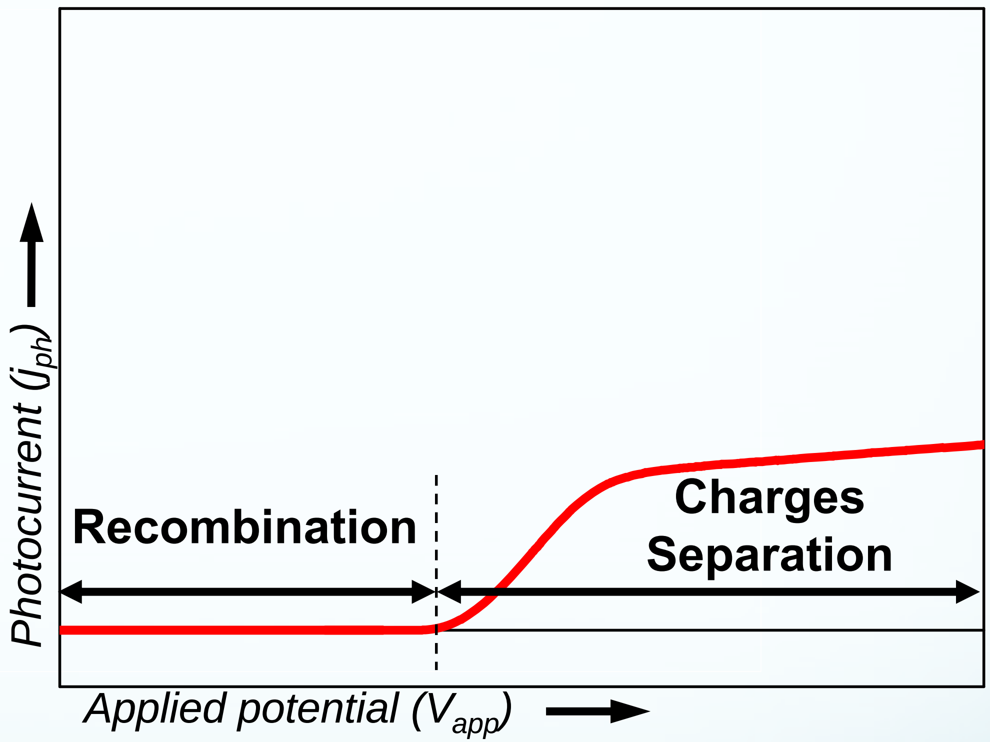
Co-alloying concept





Photoelectrochemical appro





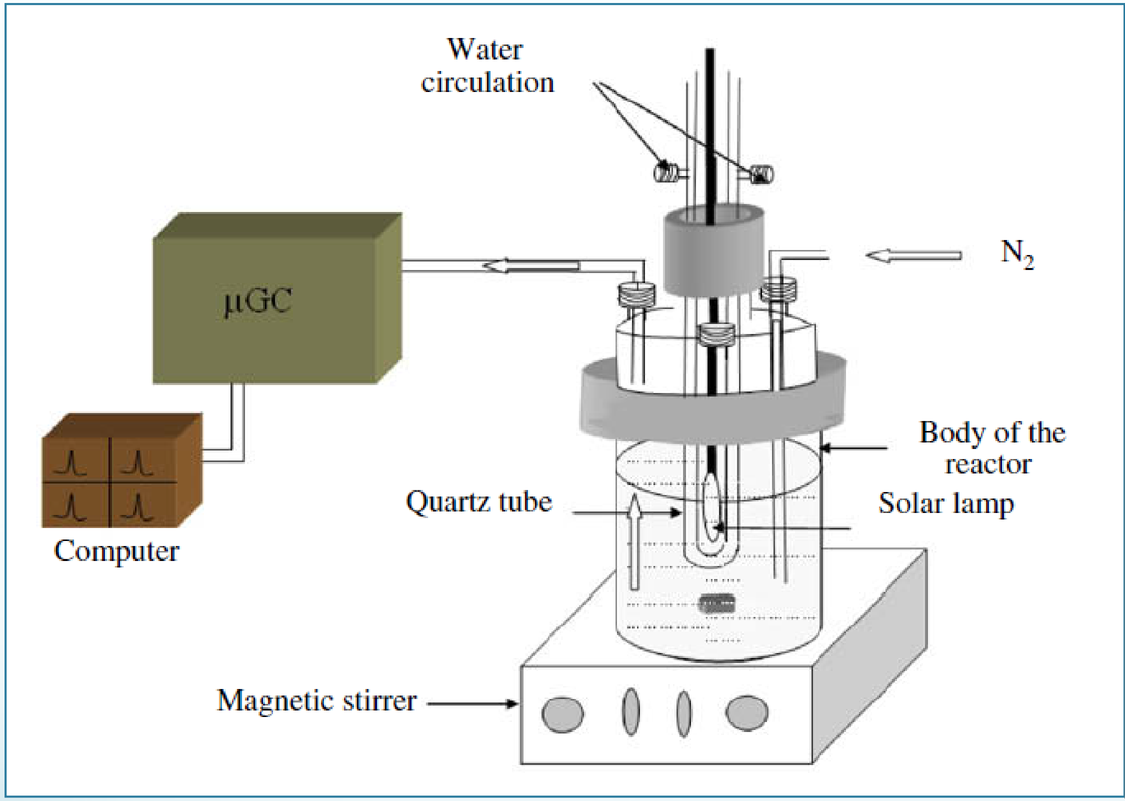
$$\eta = \frac{j_{ph}(1.23 - V_{app})}{P_{lum}}$$

- Reaction products separation (gaz)
- Separation of the different functions
- Separation of charge carriers

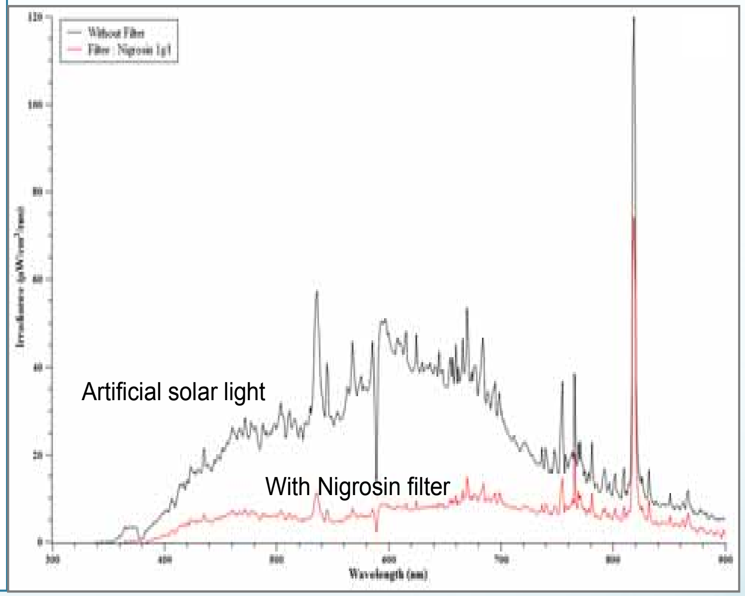
V_{app} Electrochemichal ≈ 1.8 V

V_{app} Photoelectrochemical ≈ 0.2 V

Photocatalytic approach



Spectre d'émission



Volume : 1l

Solar or visible light tirradiation

N_2 flow rate: between 50 and 500 mL/min

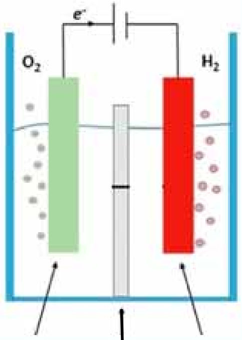
Photocatalyst weight: between 100 mg and 500 mg

Temperature : controlled between 18°C and 25°C

On-line gaseous products analysis

Photocatalytic *vs.* photoelectrochemical configuration

Photoelectrochemical (PEC)



Photoanode Membrane (Photo)cathode

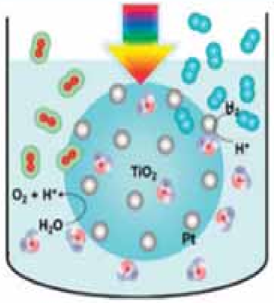
Drawbacks

- ✓ Photocatalyst immobilisation onto electrodes ➡ limitation for large scale applications ?
- ✓ Use of small amounts of photocatalyst ➡ limited performance (H_2 production)
- ✓ Use of membranes ➡ costs increase ?

Avantages

- ✓ Moderate efficiency
- ✓ Separated H_2 and O_2 evolution

Photocatalytic (PC)



Suspended nanoparticles reactor

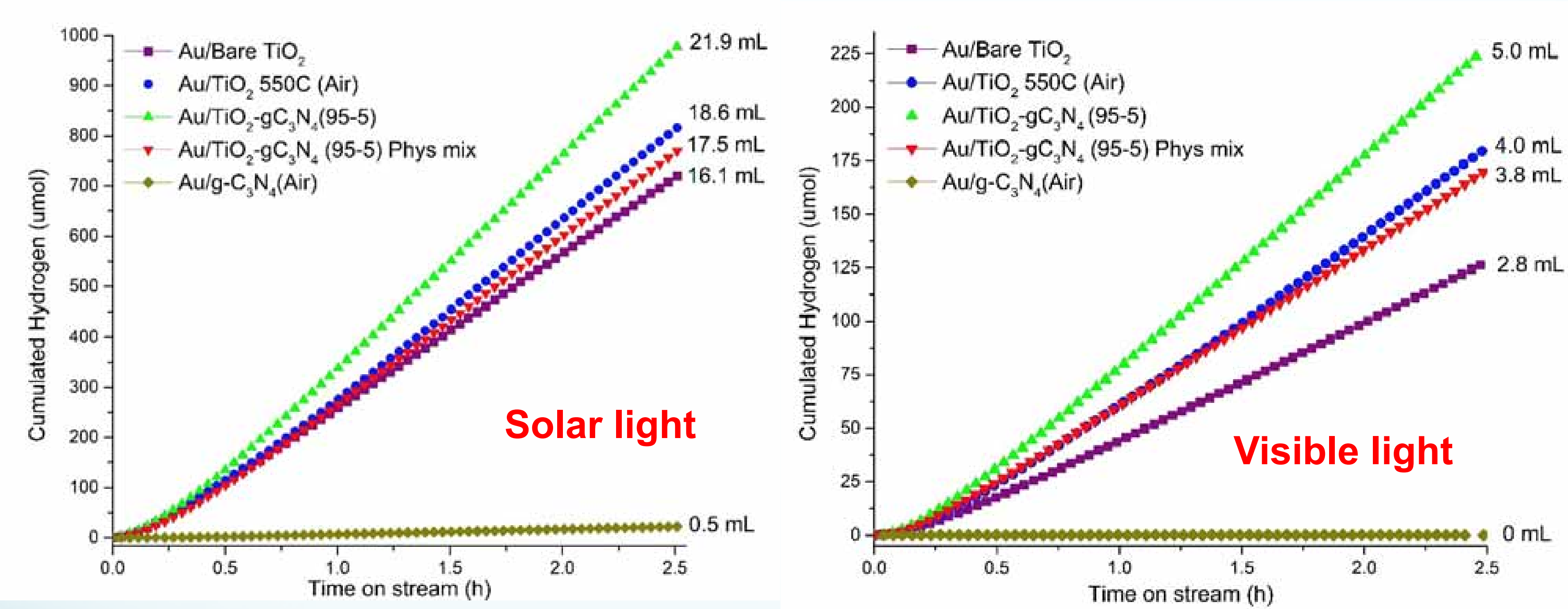
Drawbacks

- ✓ Lower efficiency than PEC
- ✓ Use of sacrificial agent addition

Avantages

- ✓ No need for photocatalyst immobilisation
- ✓ It is thus possible to use larger amount of photocatalyst
  ➡ higher performance (H_2 production)
- ✓ Possibility of use of liquid organic pollutants as sacrificial agent

H_2 production performance Amount of evolved H_2



Under artificial solar light (mainly UV+Vis) irradiation: 22 mL of evolved H_2 over 2.5 h at room temperature by using exclusively light

➢ Under artificial Vis light irradiation: 5 mL of evolved H_2 over 2.5 h at room temperature by using exclusively light

Conclusion

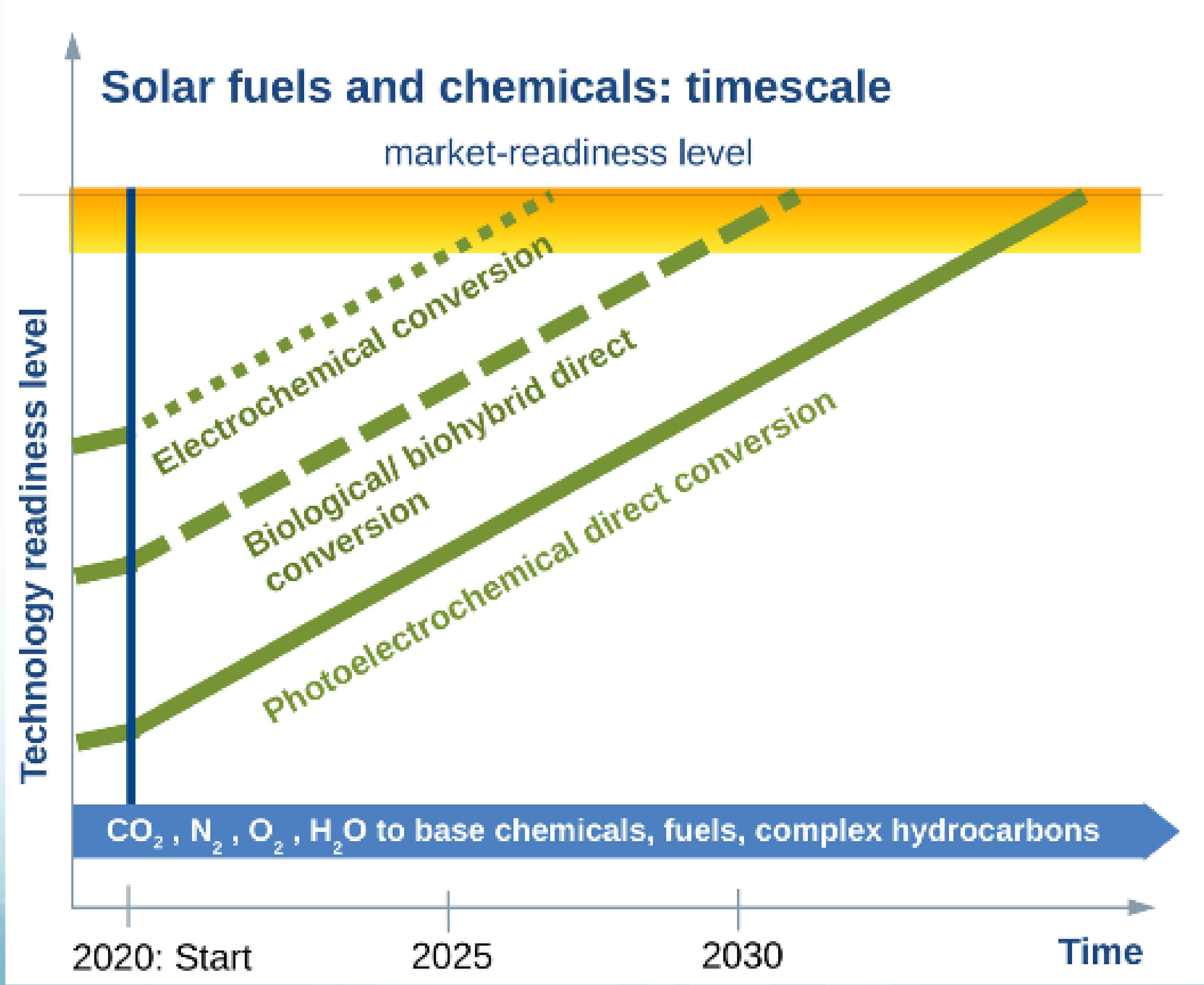
- **Rational design of photocatalytic composites for non-carbon based H_2 production :**
  - Separate optimisation of the different functions
  - Synergy effect
  - Easy synthesis and moderate cost photocatalysts

- **Complementary technology for H_2 production only based on**
  - Light activation
  - Working at room temperature
  - No other energy input (heat, pressure, …)

- **Scalable technology**

- **Coupled to CO_2 photoreduction**
  Mimicking artificial photosynthesis

Conclusion


Solar fuels and chemicals: timescale
market-readiness level
Technology readiness level
Electrochemical conversion
Biological/ biohybrid direct conversion
Photoelectrochemical direct conversion
CO_2 , N_2 , O_2 , H_2O to base chemicals, fuels, complex hydrocarbons
2020: Start
2025
2030
Time

Aknowledgements

INVESTISSEMENTS D'AVENIR

ifp Energies nouvelles

Région Alsace

AGENCE NATIONALE DE LA RECHERCHE ANR

FONDATION AIRBUS GROUP

Université de Strasbourg

MAKE OUR PLANET GREAT AGAIN

SUNCO2H2Energy project 2018

Konstantinos Christoforidis


Thank you for
your attention
e⁻
2H⁺ + 2e⁻ → H₂
hν
h⁺
H₂O + 2h⁺ → ½ O₂ + 2H⁺

Remerciements

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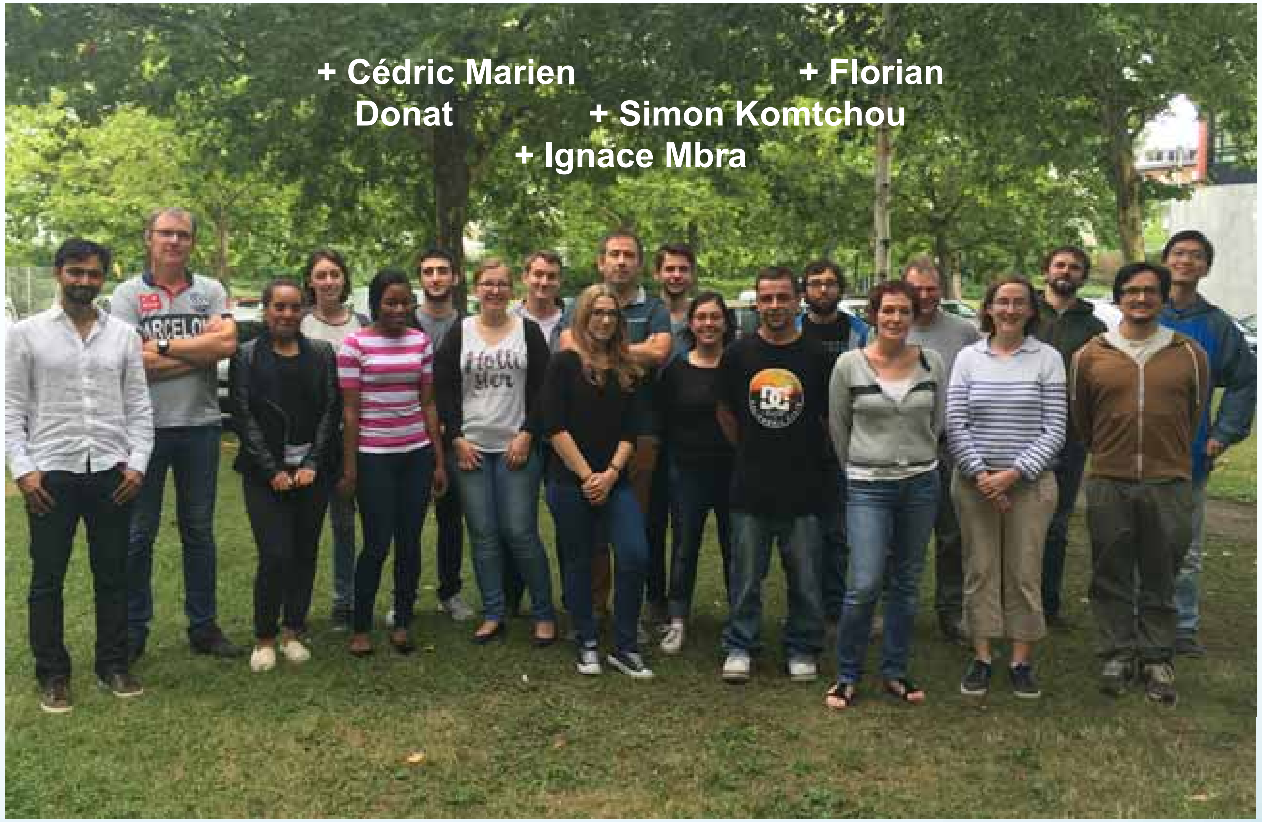

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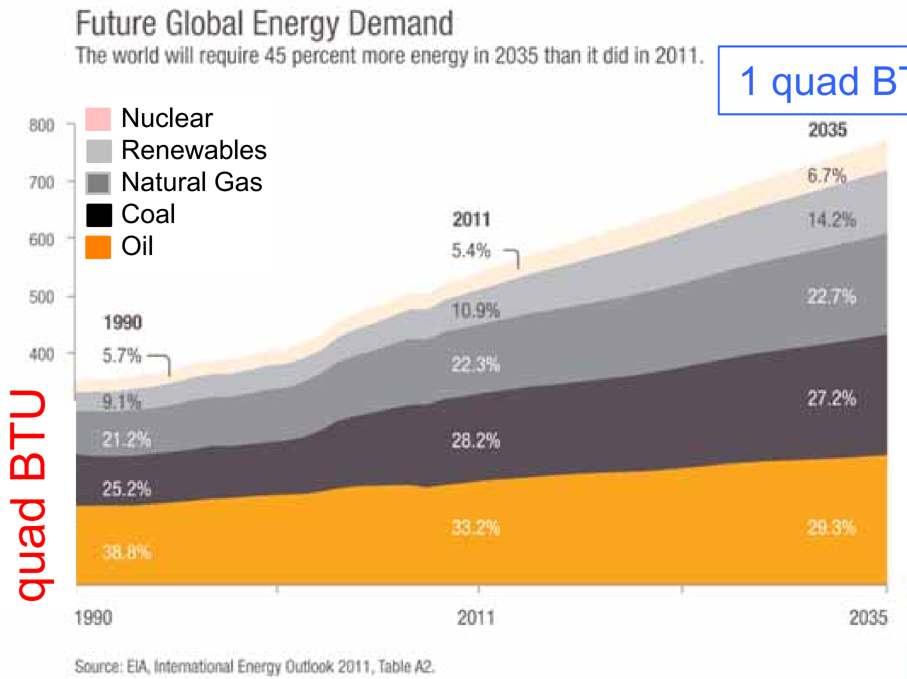
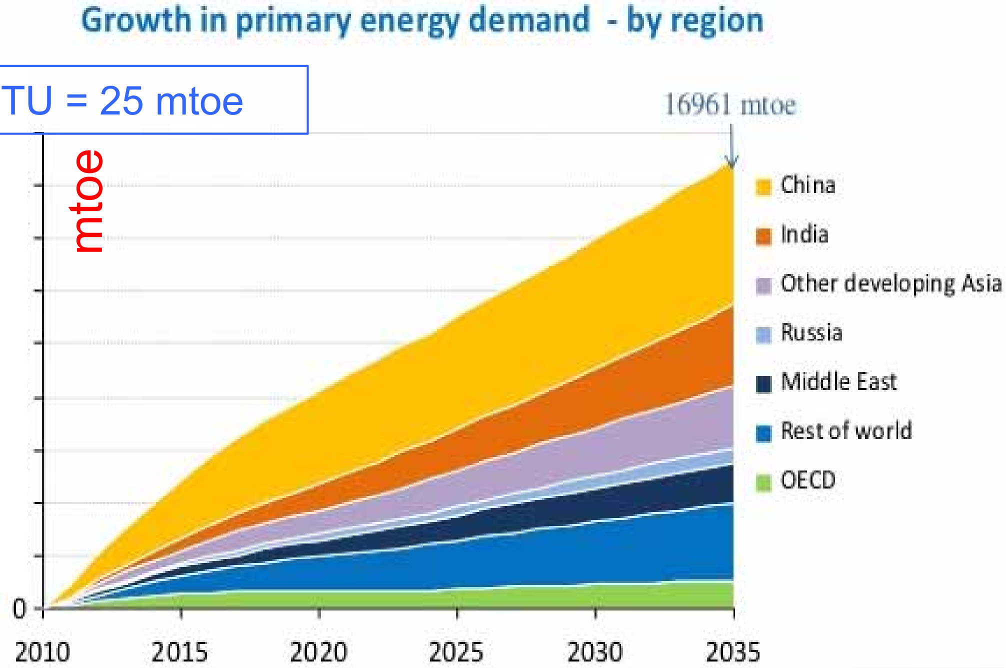
The global Energy challenge



1 quad BTU = 25 mtoe



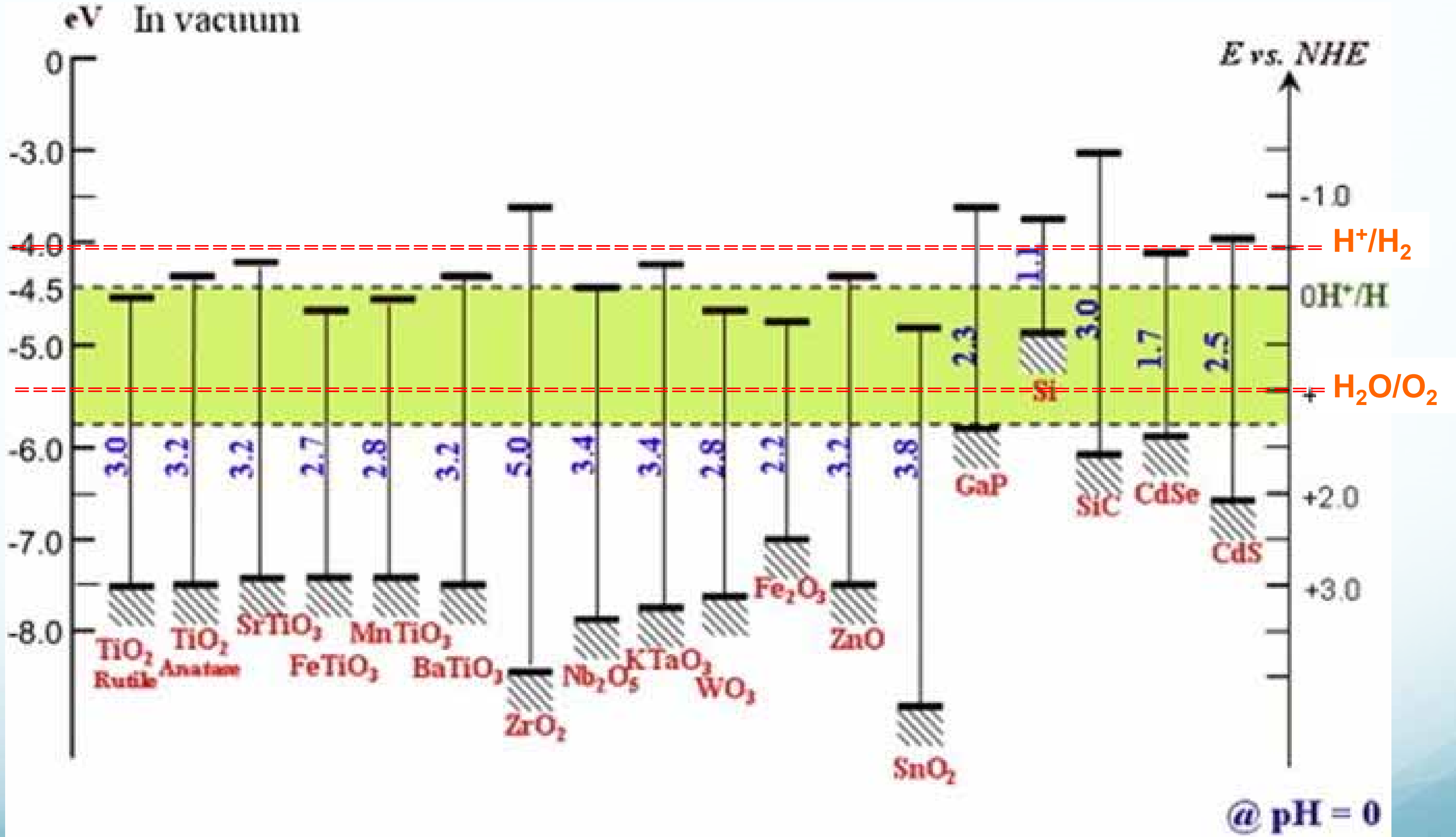
BTU = British Thermal Unit
1 quad BTU 10^{15} **BTU** = $1,055 \times 10^{18}$ J

Toe = **tonne of oil equivalent** defined as the amount of energy released by burning 1 tonne of crude oil = 4.2×10^{10} J
1 mtoe = $4,2 \times 10^{16}$ J

- Global energy demand increases by one-third from 2010 to 2035
- China & India accounting for 50% of the growth
- 80% of global energy demand is issued from fossile sources

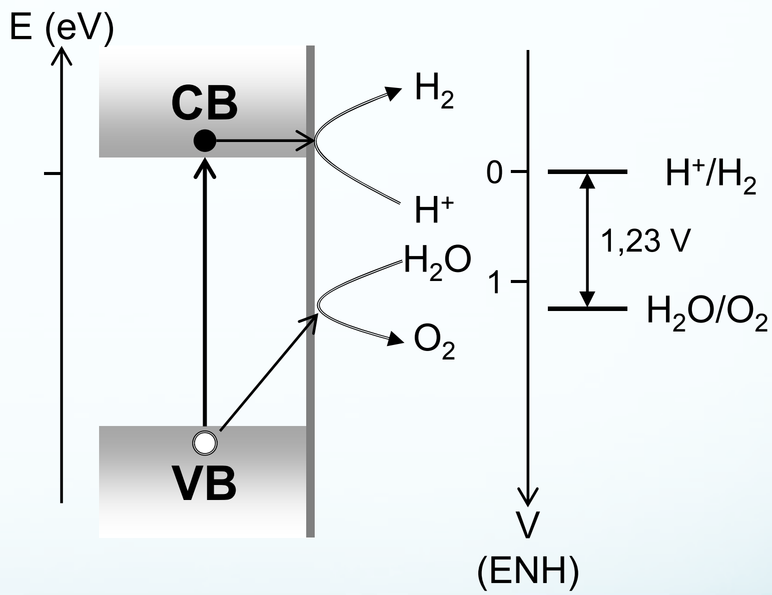
Concept of a circular economy of carbon using solar energy input and atmospheric gases as feedstocks

What kind of material ?



Conditions (necessary but not sufficient)

- Band edges position
  - Valence band of SC more positive than potential O_2/H_2O
  - Conduction band of SC more negative than potential H^+/H_2

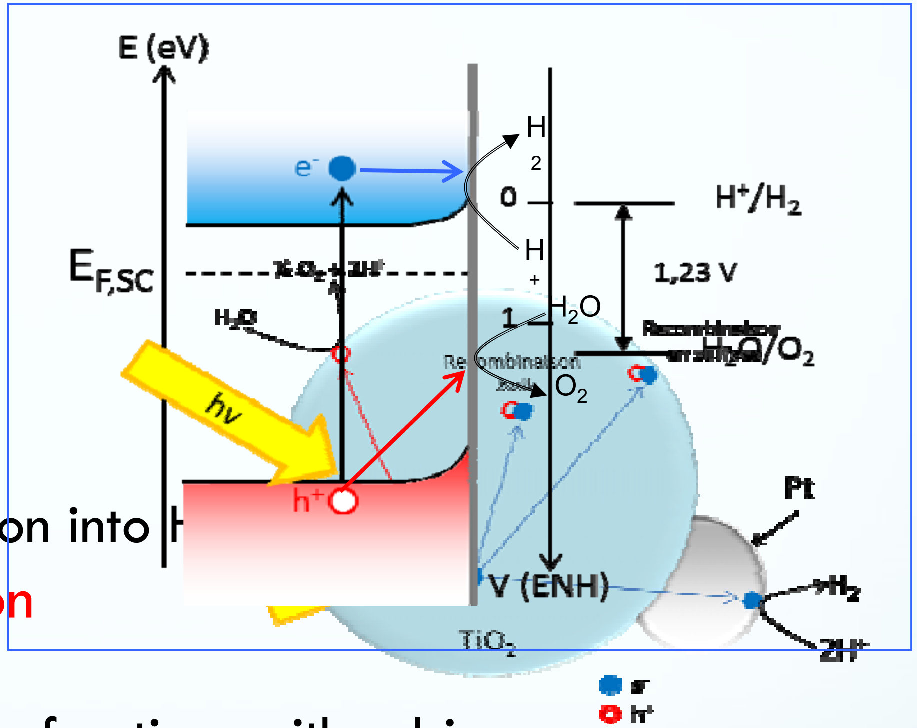


In theory favorable with TiO_2

Limitations and bottlenecks

- Kinetic overpotential and thermodynamic losses

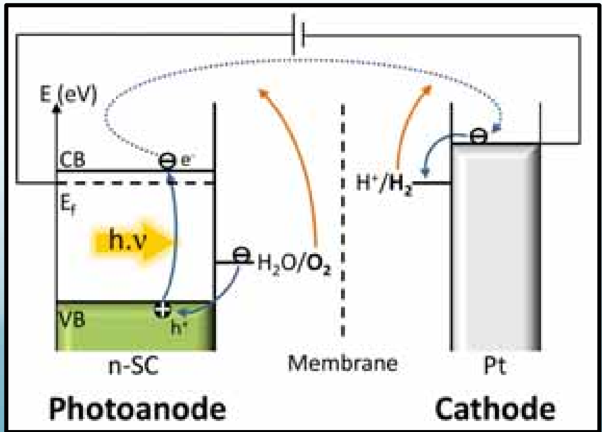
0,3 V for water-splitting



- Addition of co-catalyst (H^+reduction into H

Photocatalytic configuration

- Separation of anodic and cathodic functions with a bias

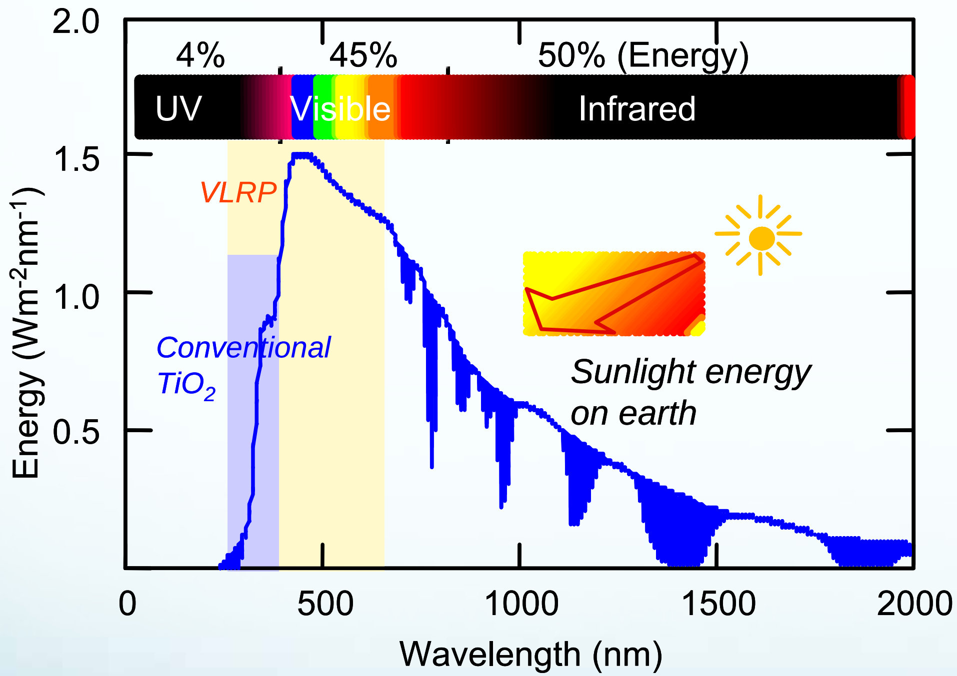


PhotoElectroChemical configuration

Limitations and bottlenecks

➢ Light absorption

- Absorption of a maximum of « solar » photons



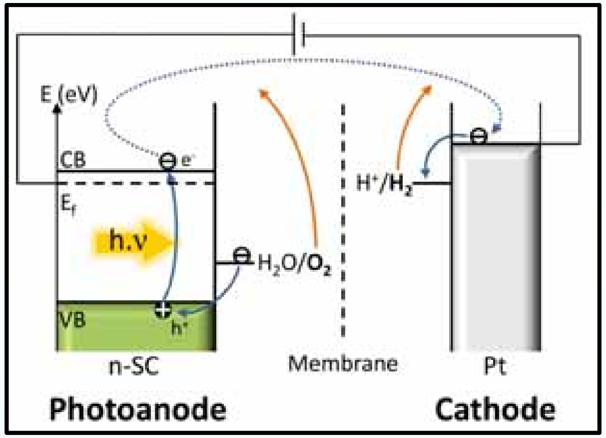
TiO_2 anatase : only 3-4% solar spectra

- ➢ Chemical doping (cationic, anionic, co-doping)
- ➢ Heterojunction formation between TiO_2 and another SC with lower band gap
- ➢ Surface Plasmon Resonnance effect (SPIE)

➢Back reaction: $H_2 + ½ O_2 \rightarrow H_2O$

➢ Spatial separation of H_2 and O_2 products

Photoelectrochemical cell with2 compartments (cathodic for O_2 evolution and anodic pour H_2 evolution)



Photoelectrochemical cell (PEC)

➢ « Hinder » one half-reaction Photocatalytic (PC)

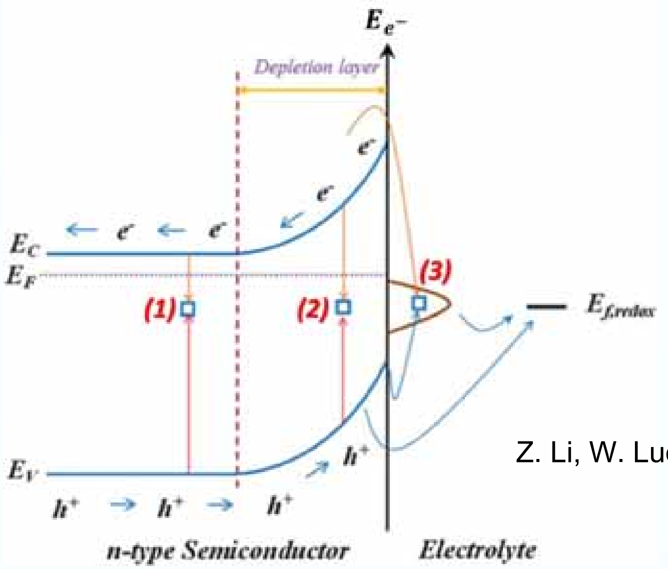
Addition of sacrificial agents (é donors), ex: Methanol, Triethanolamine,…

- Only H_2 evolution

Addition of sacrificial agents (é acceptors), ex: $AgNO_3$

- Only O_2 evolution

➢Charges recombinations

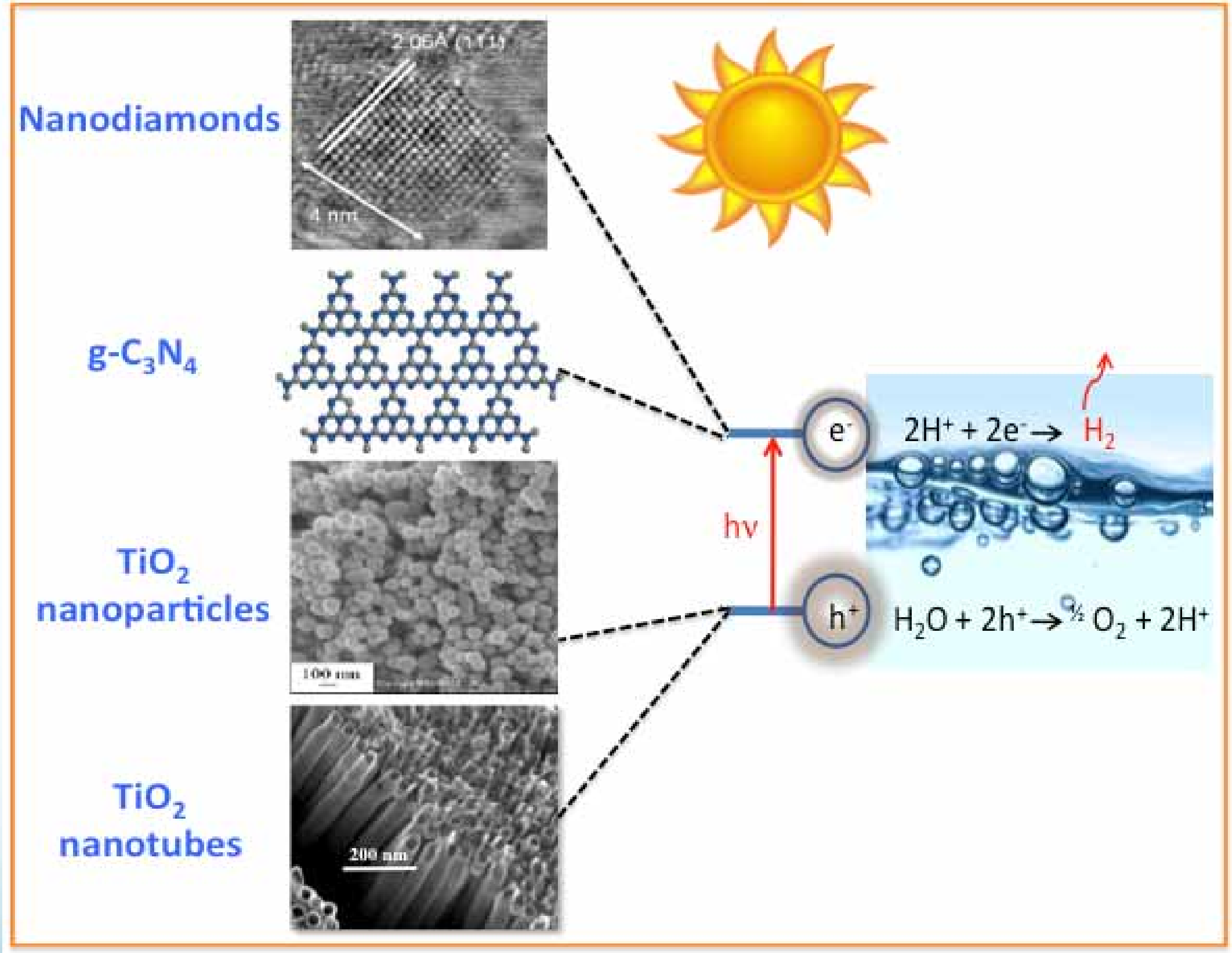


Recombinations in the bulk, inside of the depletion layer or on the surface

Z. Li, W. Luo, M. Zhang, J. Feng, Z. Zou, *Energy & Environmental Science* 6, 347 (2013)

- Introduction of charge traps (addition of metallic nanoparticles)
- Chemical doping (cationic, anionic, co-doping)
  Increase of conductivity and charge carriers mobility
- Application of a bias
- Control of the morphology (ex: nanotubes, nanorods, …)
  Dissociation direction of light absorption/minority charge carriers

Some examples from ICPEES

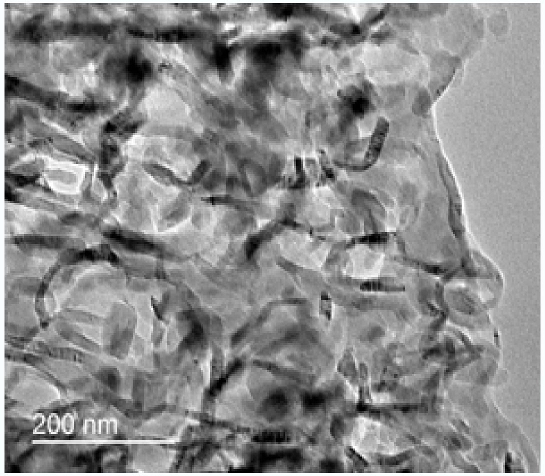


- ➢ Heterojunction formation
- ➢ Chemical doping (co-doping approach)
- ➢ Addition of (bi-) metallic NPs (Pt, Au, Ag Au-Ag, Au-Cu, Au-Ag, Au-Ni)

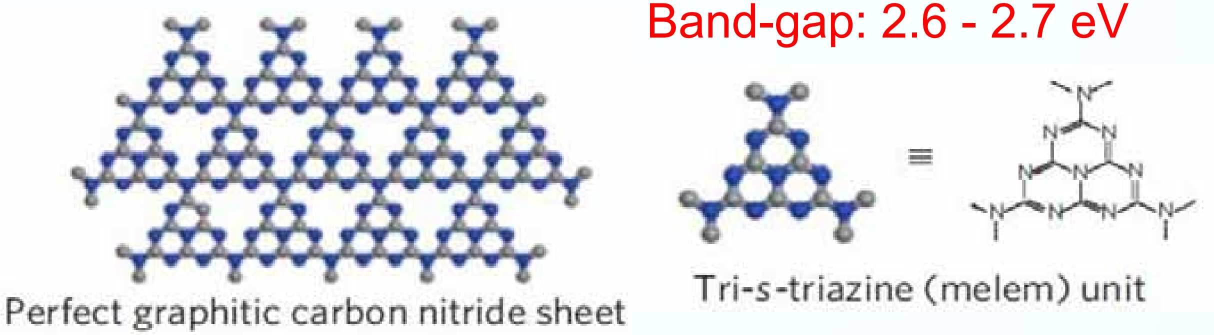
Au/gC_3N_4-TiO_2 Composites

PhD Clément Marchal, 3 March 2017

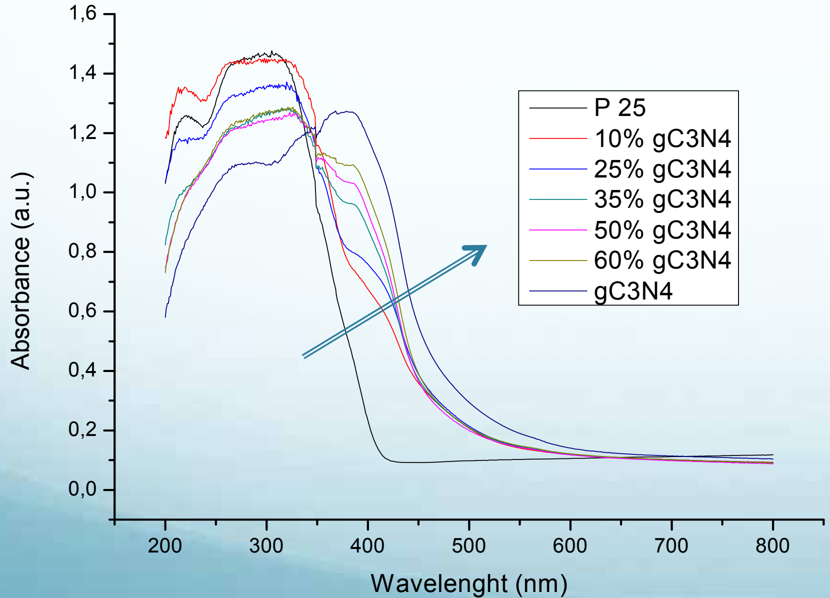
PhD Pablo Calvo, 17 June 2019



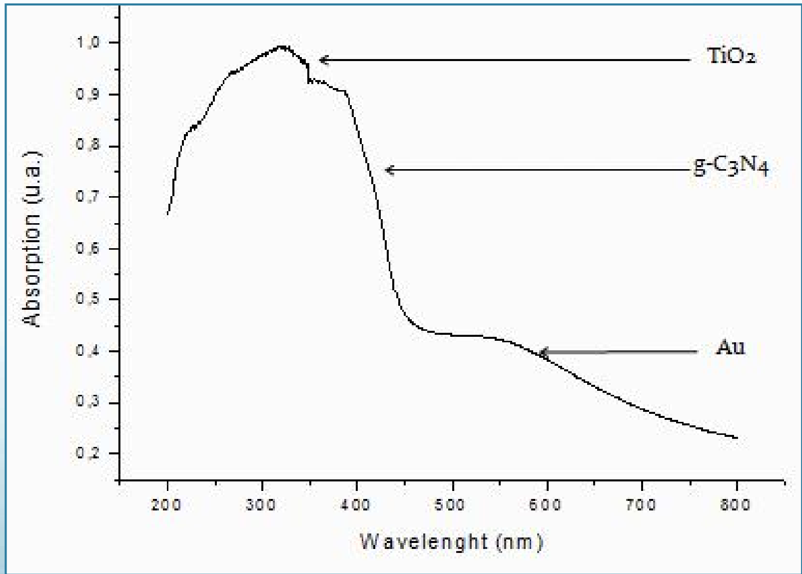
Band-gap: 2.6 - 2.7 eV



Composites gC_3N_4-TiO_2

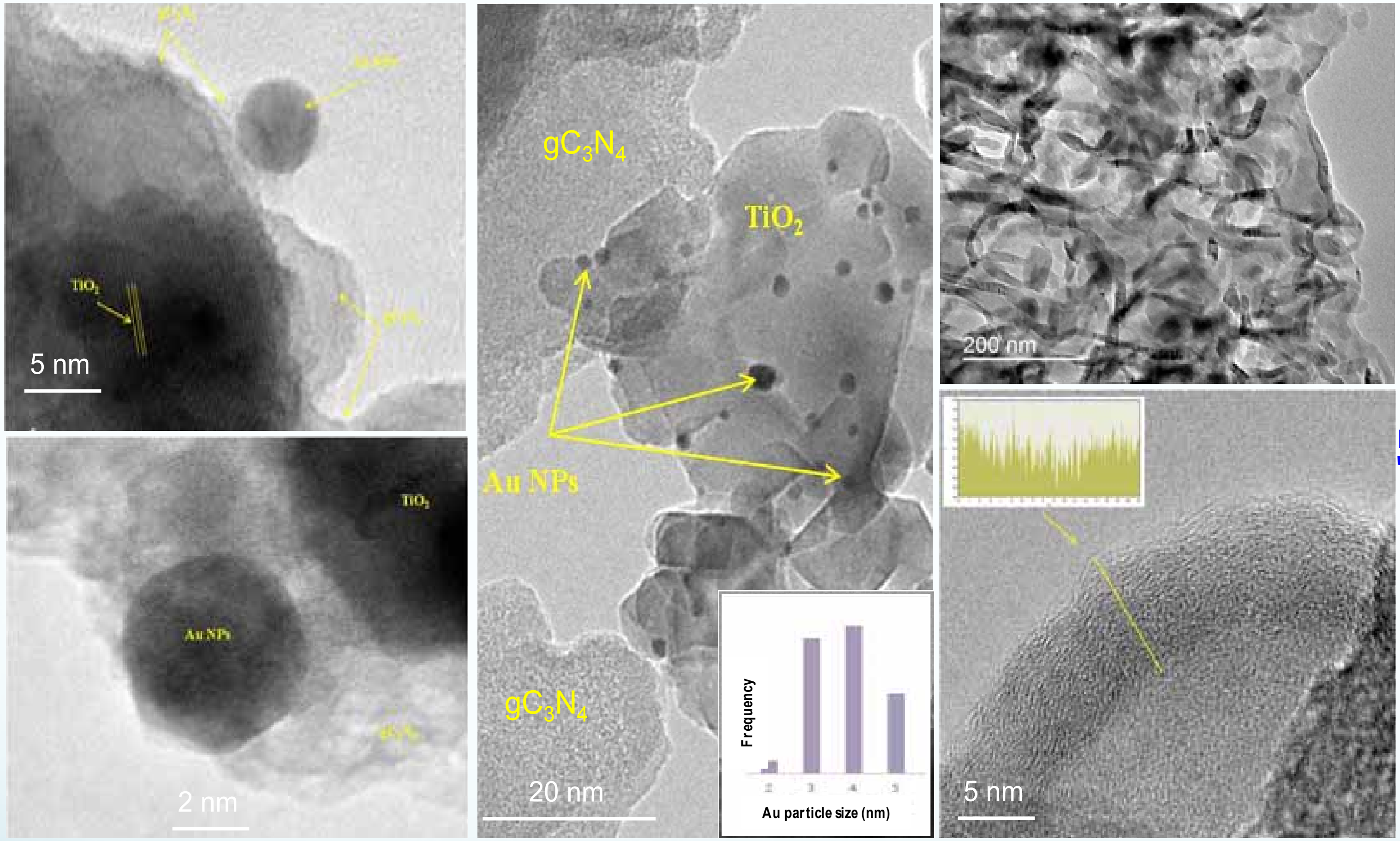


Composites Au/gC_3N_4-TiO_2



Overlap of SPIE of Au NPs with absorption range of C_3N_4

Au/gC$_3$N$_4$-TiO$_2$ (P25) Composites



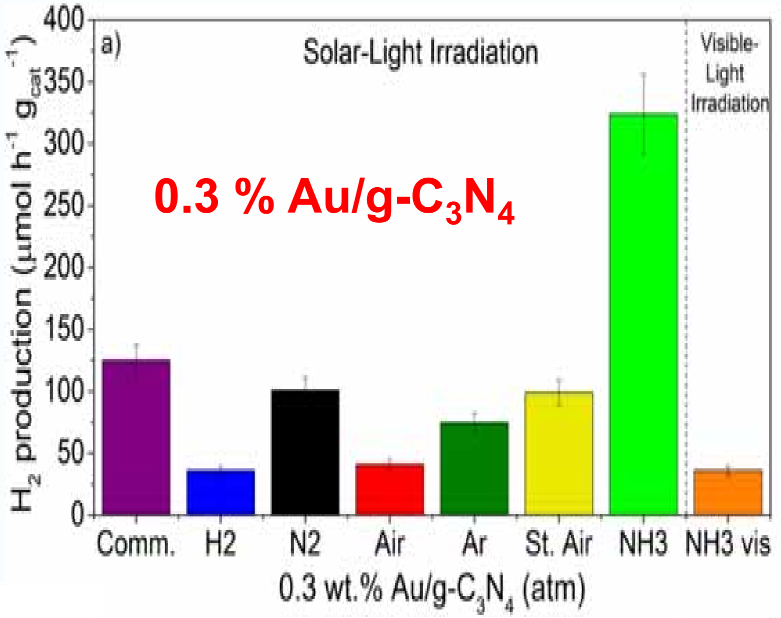
0.3 wt.% Au
5 wt.% g-C$_3$N$_4$

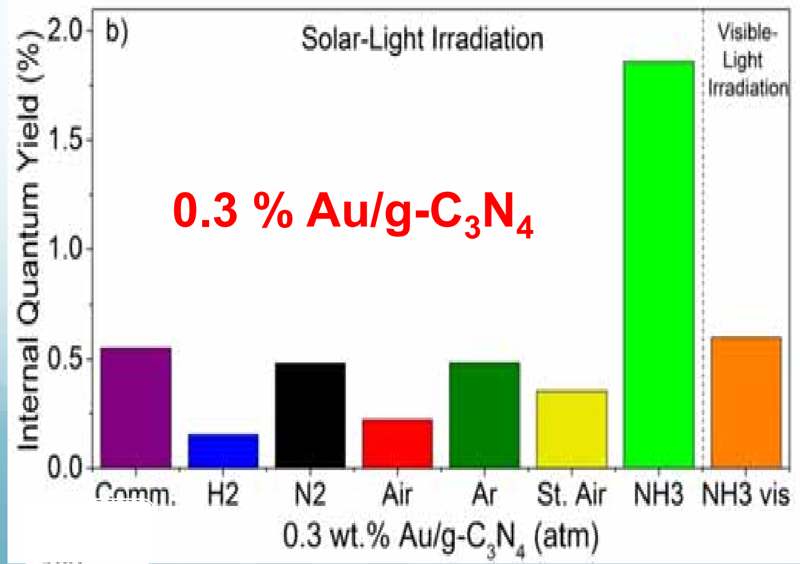
- Well-contacted interface between TiO$_2$ and gC$_3$N$_4$
- Homogeneous Au NPs deposition on TiO$_2$ and gC$_3$N$_4$
- Au NPs average size 4.7 nm, deviation 0.9 nm

Advanced Energy Materials, (2018) 1702142
C. Marchal, T. Cottineau, …, C. Colbeau-Justin, V. Caps, V. Keller

J. Mater. Chem. A, *in press*
P. Calvo,C. Marchal, T. Cottineau , V. Caps, V. Keller

H_2 production performance and quantum yield (0.3 % Au/ g-C_3N_4)





0.3 wt. % Au/g-C_3N_4-NH_3

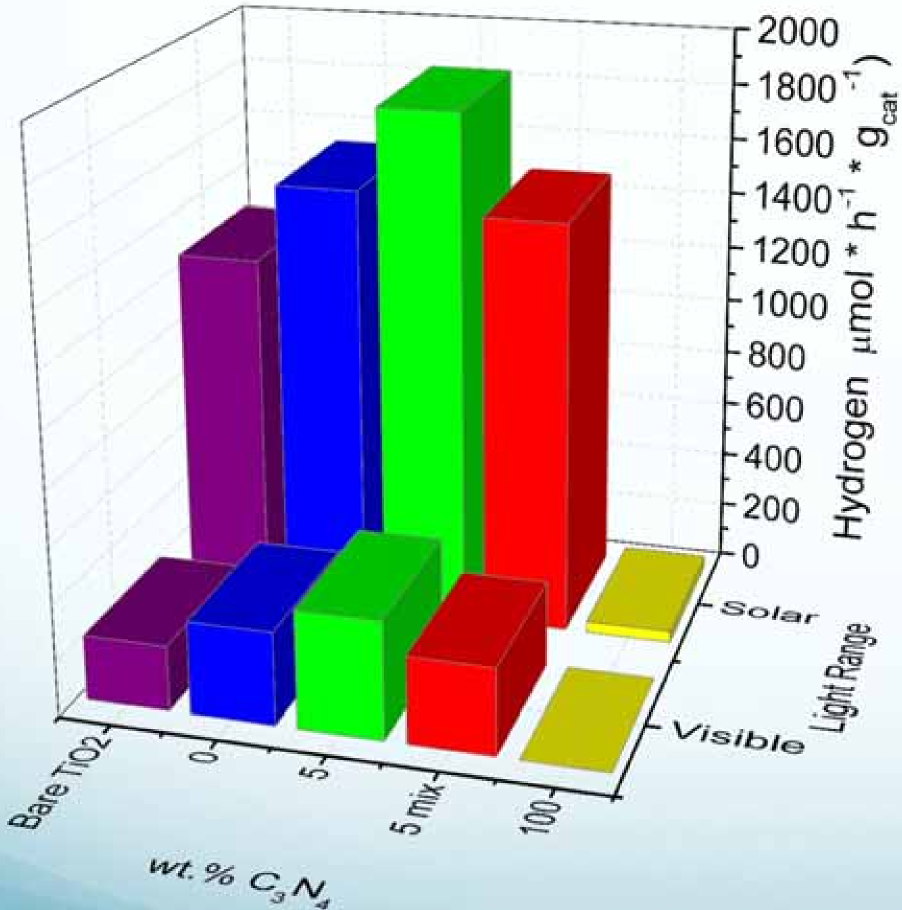
- **324** H_2 µmol h^{-1} g_{cat}^{-1} (**solar**)
- **26** µmol h^{-1} g_{cat}^{-1} H_2 produced (**visible**)

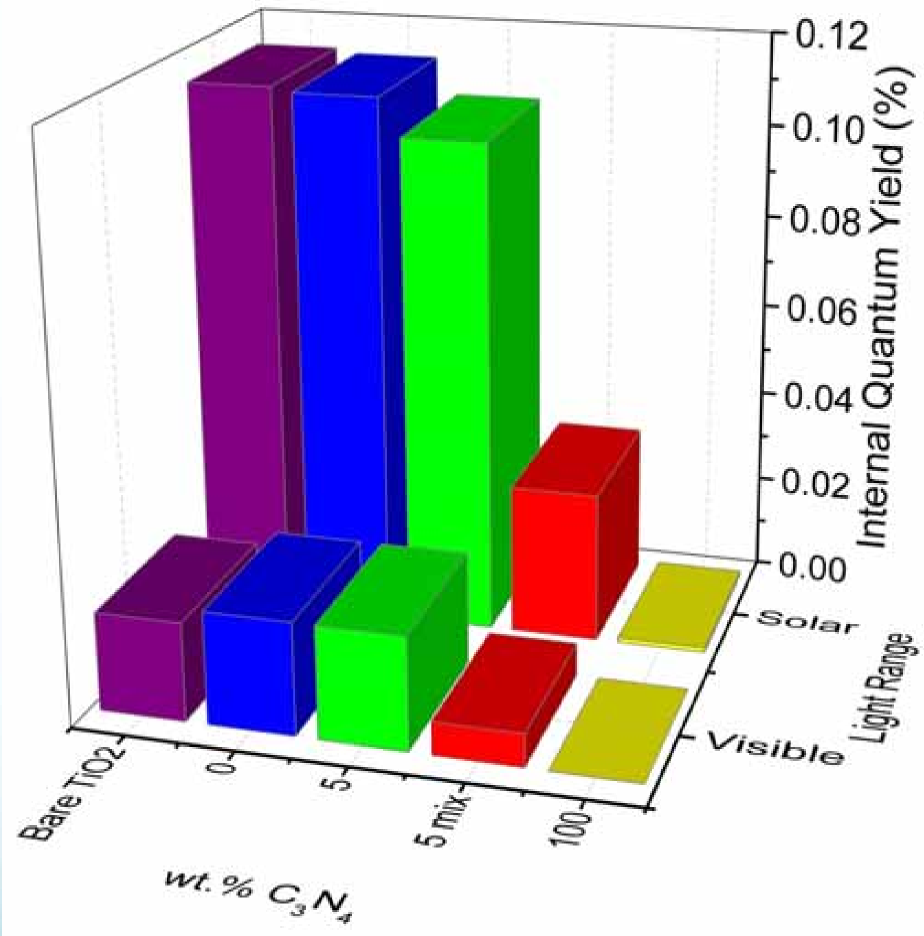
$$\varphi_I = 2 \times \frac{r_{H_2}}{q_{p(Abs)}}$$

$$q_{p(Abs)} = \int_{\lambda_{min}}^{\lambda_{max}} \frac{P(\lambda) \times (1 - 10^{A(\lambda)l})}{E(\lambda)} \, d(\lambda)$$

H_2 production performance (0.3 % Au/TiO_2-gC_3N_4)

5 mix (red) = Physical mixture of 5%[0.3%Au/g-C_3N_4] + 95% [0.3%Au/TiO_2 (P25]

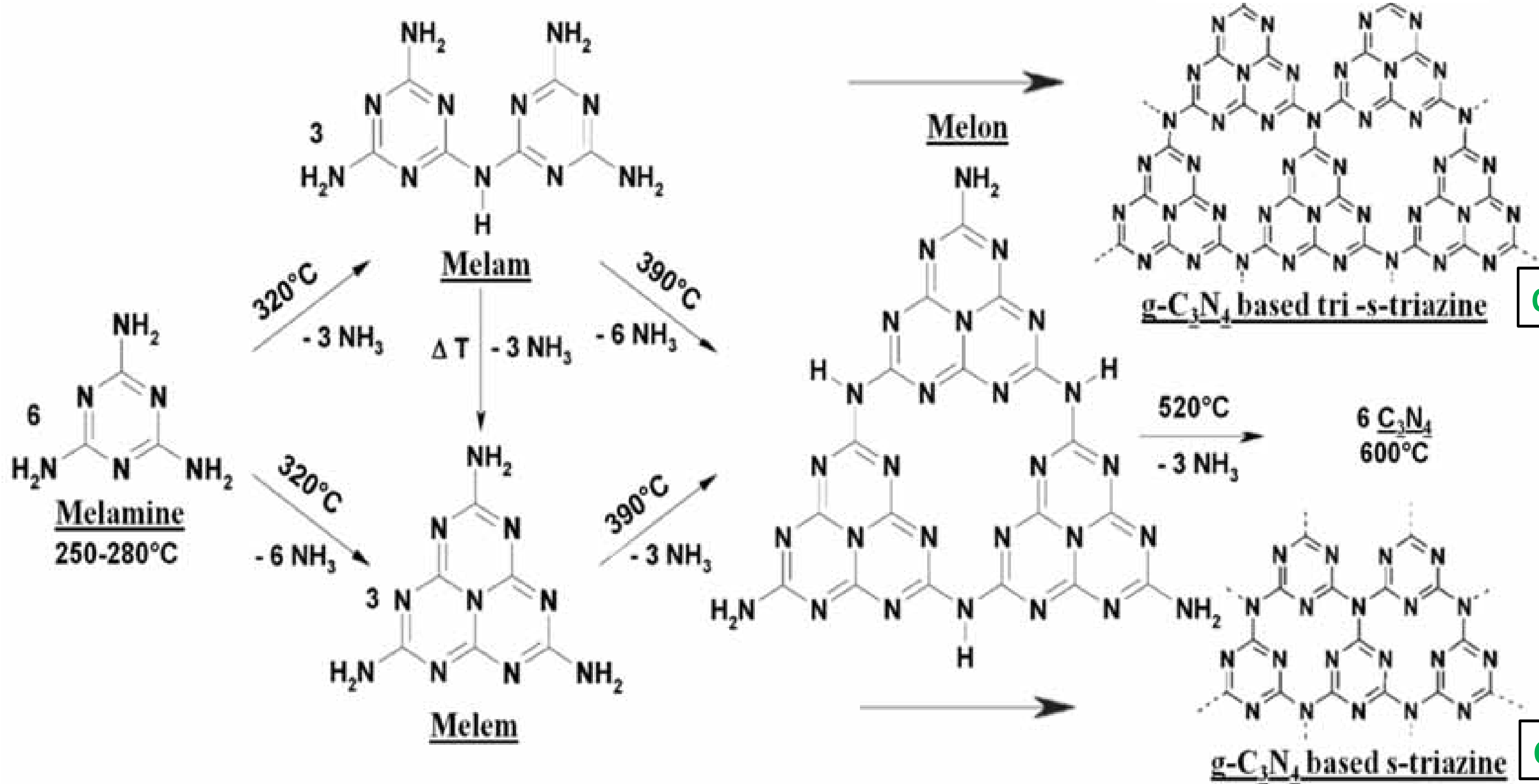




- H_2 production enhancement for the composite in comparison to references and physical mix in both solar and visible light range
- Light absorption is not the only parameter contributing to the material's activity

Formation mechanism of graphitic Carbon Nitride (g-C_3N_4)

Perfect g-C_3N_4 sheet



CNTST

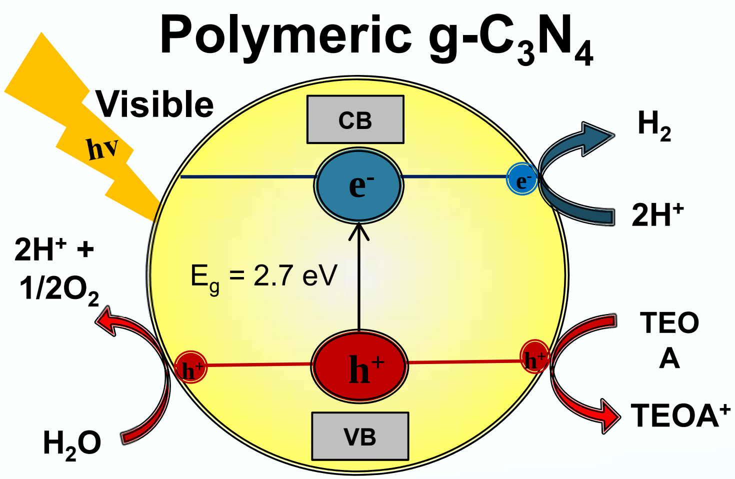
CNST

Jürgens *et al*, Melem (2,5,8-Triamino-tri- s -triazine), an Important Intermediate during Condensation of Melar[illegible]ngs to Graphitic Carbon Nitride: Synthesis, Structure Determination by X-ray Powder Diffractometry, Solid-State NMR, and Theoretical Studies, J[illegible]em. Soc. 125 (2003) 10288–10300

Improvement of gC_3N_4 based materials ?

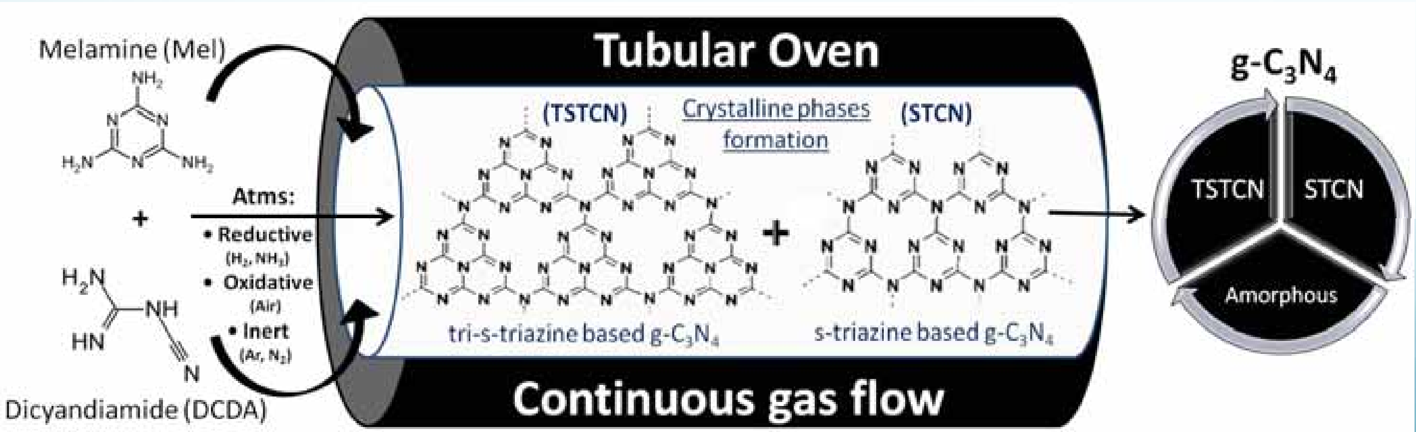
Advantages of $g\text{-}C_3N_4$
Medium band gap
2D Mesoporous
CB & VB positions

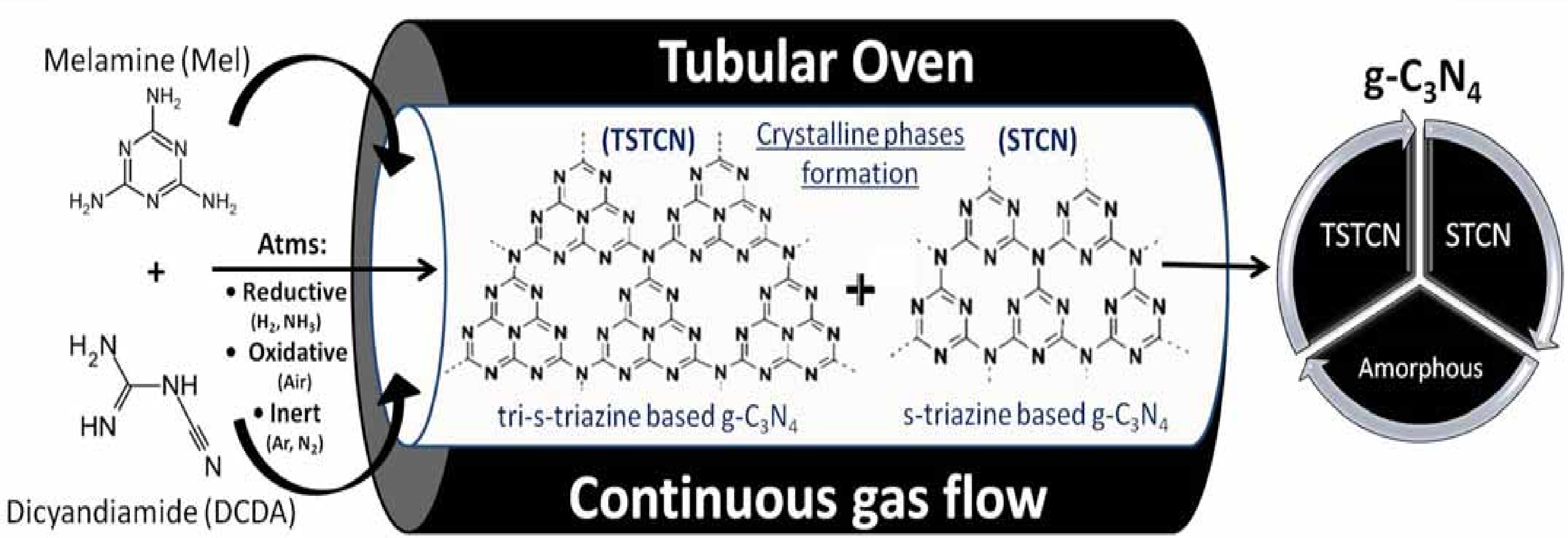
Drawbacks of $g\text{-}C_3N_4$
Low surface area
Rapid recombination



Antonietti *et al*, Nat. Mat. (2009)

(1) Tune synthesis atmosphere

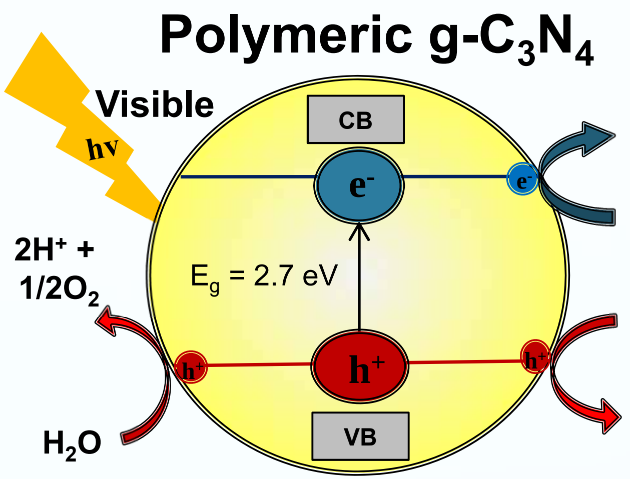



Melamine (Mel)
Dicyandiamide (DCDA)
Atms:
• Reductive (H2, NH3)
• Oxidative (Air)
• Inert (Ar, N2)
Tubular Oven
(TSTCN)
Crystalline phases formation
(STCN)
tri-s-triazine based g-C3N4
s-triazine based g-C3N4
Continuous gas flow
g-C3N4
TSTCN
STCN
Amorphous

Improvement of gC_3N_4 based materials ?

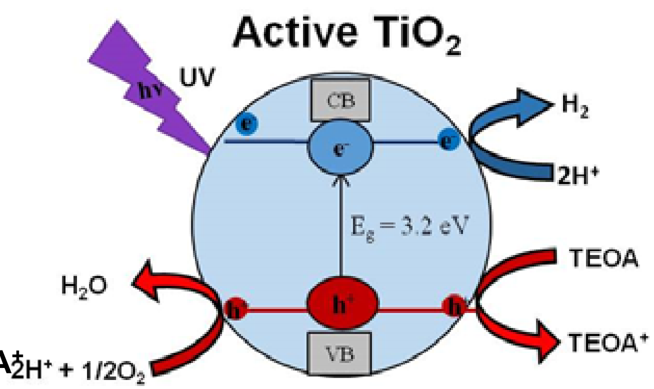
Advantages of $g\text{-}C_3N_4$
Medium band gap
2D Mesoporous
CB & VB positions

Drawbacks of $g\text{-}C_3N_4$
Low surface area
Rapid recombination



Antonietti *et al*, Nat. Mat. (2009)

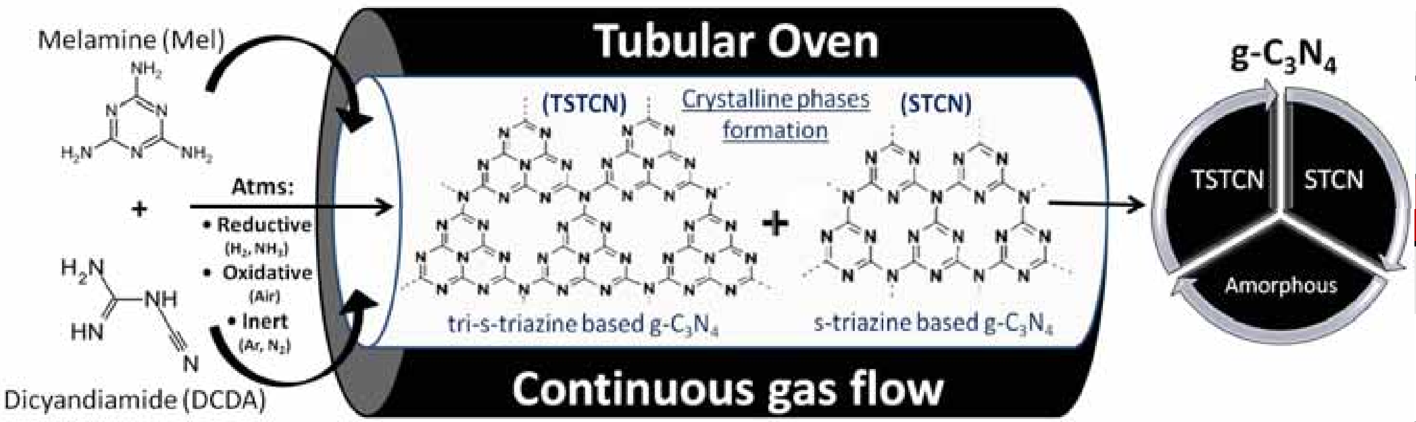
(2) Coupling with TiO_2



Advantages of TiO_2
Abundant
Chemically stable
Reasonable cost

Drawbacks of TiO_2
Wide band gap (UV)
Poor H^+ photo reduction

(1) Tune synthesis atmosphere

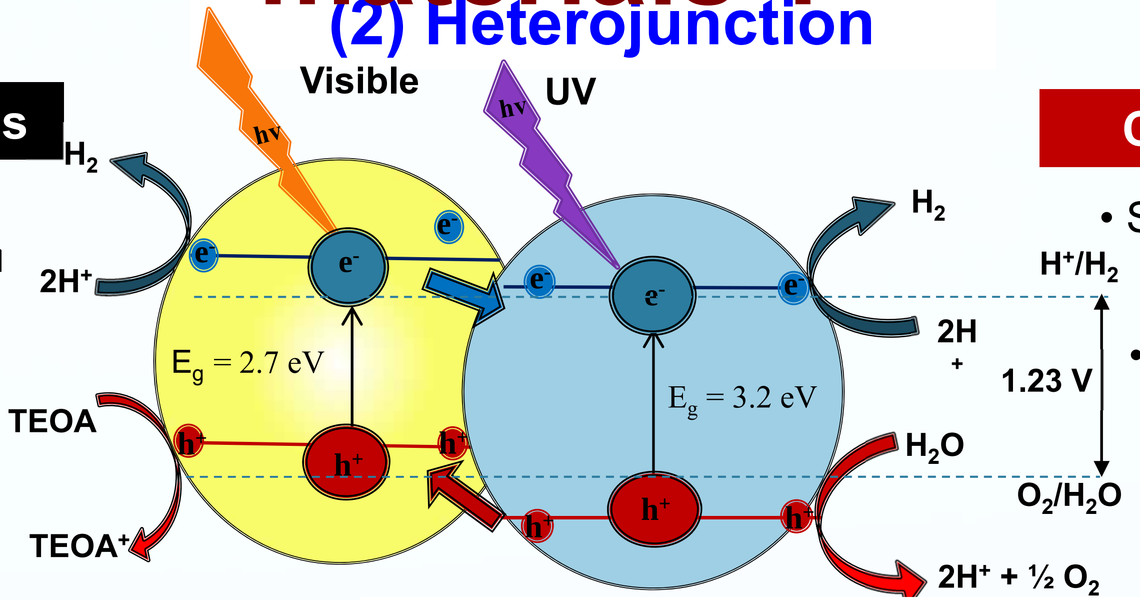


Improvement of gC_3N_4 based materials ?

(2) Heterojunction

Advantages

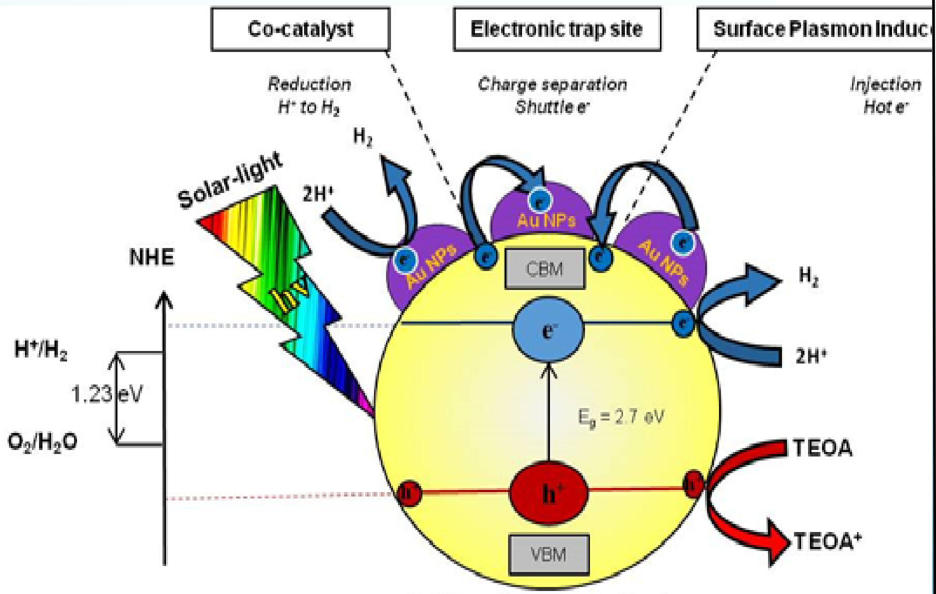
- Photosensitization of TiO_2 (Vis)
- Increase charge separation



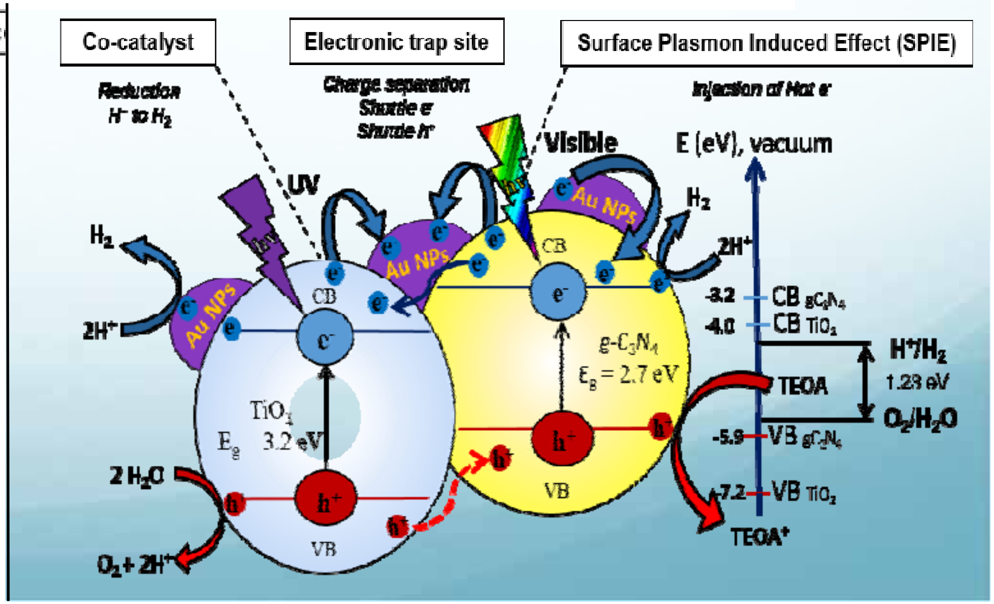
Challenges

- Synthesis method
- Good interface contact
- Optimal proportion

(1) Atm approach



(3) Au NPs deposition



Kinetics of charge carriers

Collaboration with Prof. Christophe Colbeau & Dr. Mohamed Nawfal (LCP), Université Paris Sud

TRMC (time-resolved measurement) gives changes in microwave absorption resulting from the **production** and **decay** of mobile free electrons

$$\frac{\Delta P(t)}{P} = A\Delta\sigma(t) = Ae\sum_i \Delta n_i(t)\mu_i$$

ΔP (t): Difference of microwave power reflected

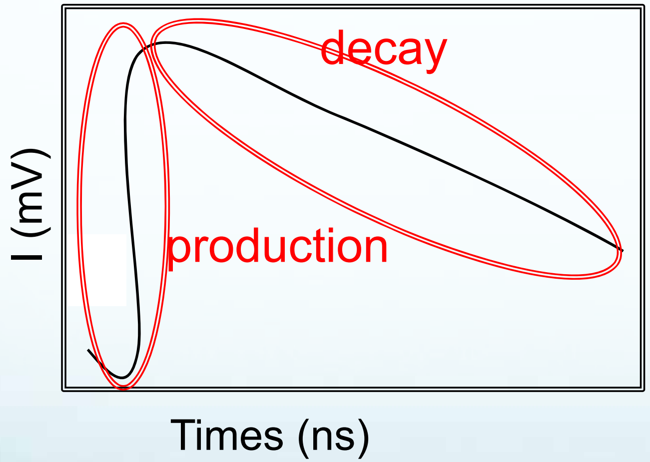
Δσ: Difference of conductivity after excitation

Δn_i : Number of excess charge carriers

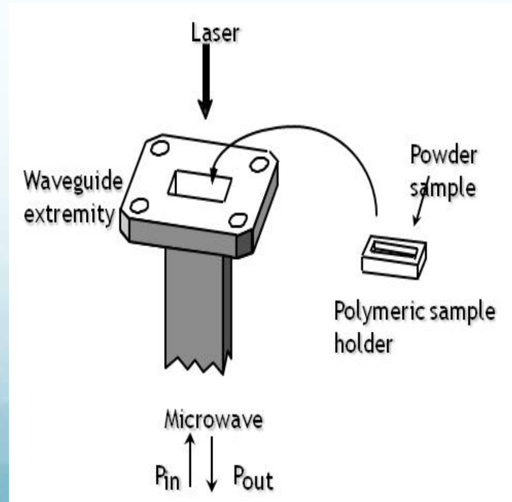
μ_i : Electyron mobility

A : Sensibility factor

- mobility of free e^-
- concentration of free e^-

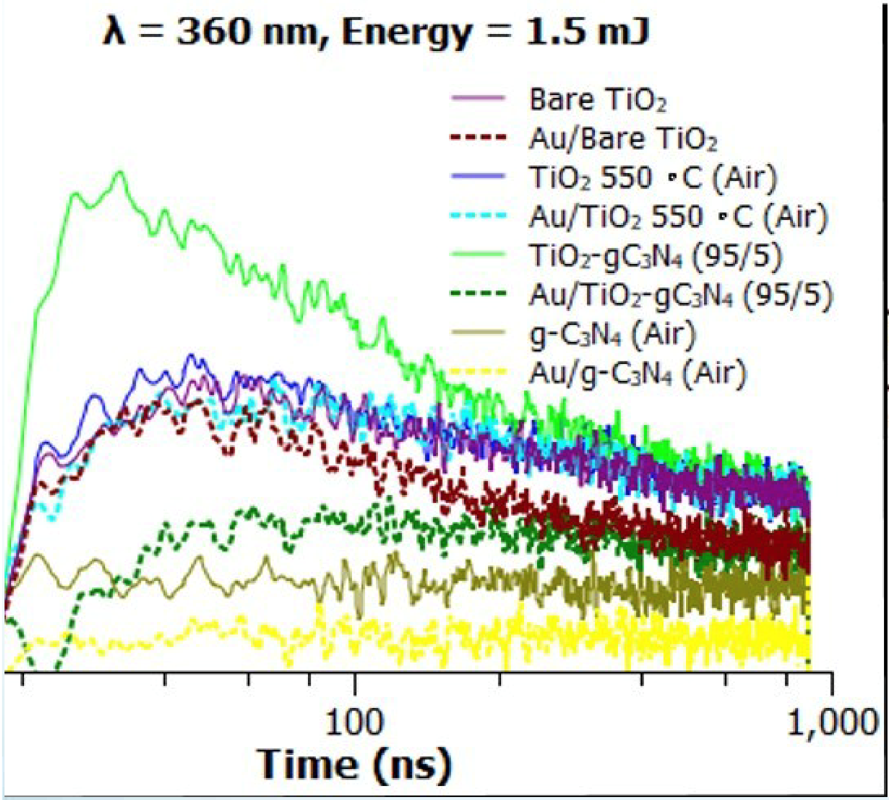


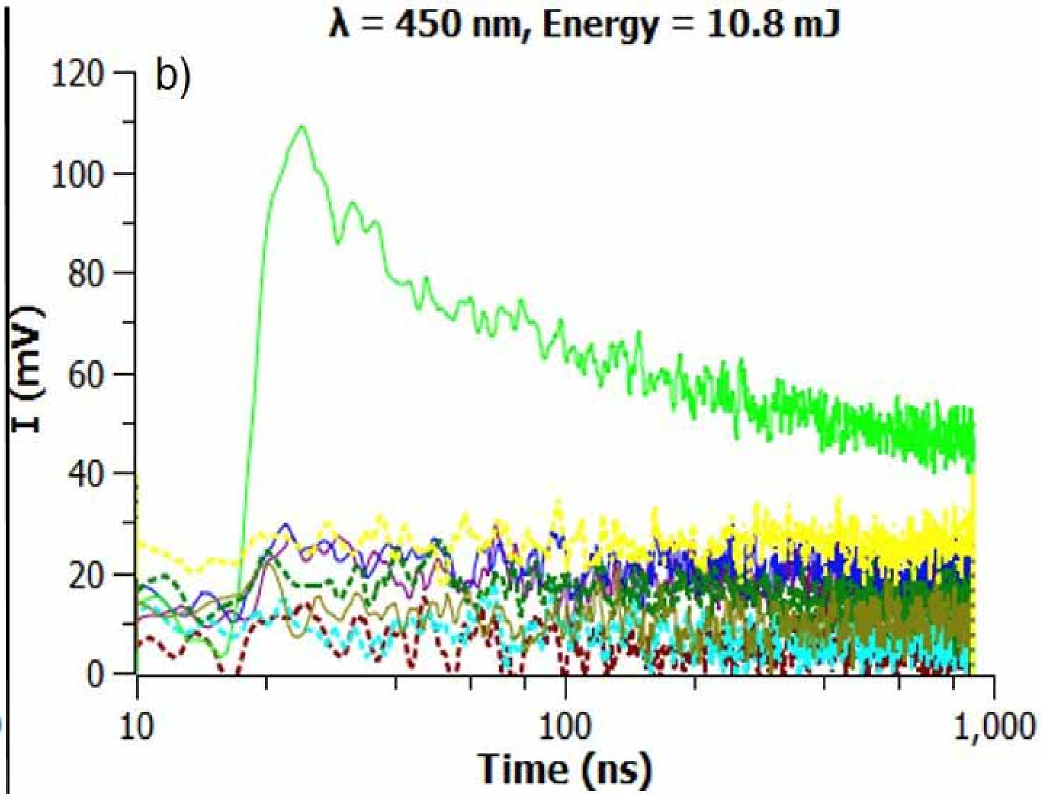
- Free electrons lifetimes
- Electron trapping
- Elecron recombination dynamics



Kinetics of charge carriers (TRMC)

Collaboration with Prof. Christophe Colbeau & Dr. Mohamed Nawfal (LCP), Université Paris Sud

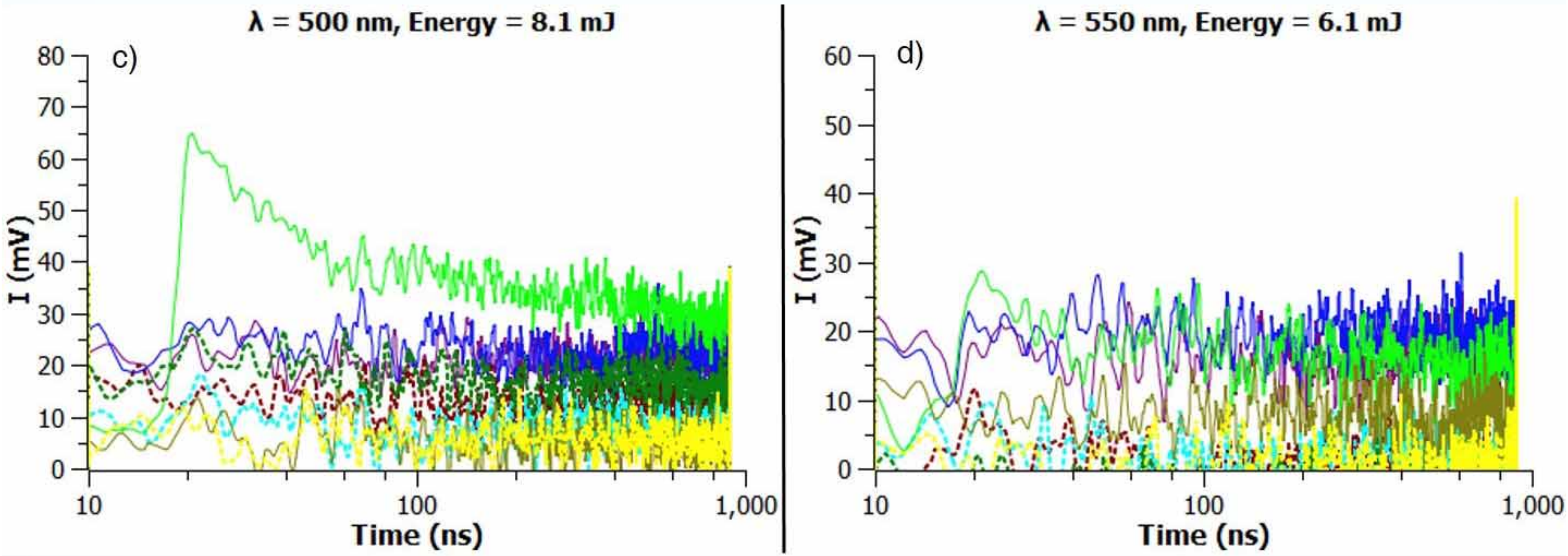




- Composite generates the highest mobile electron carriers concentration
- Au NPs act as electron trapping sites
- $g\text{-}C_3N_4$ does not generate any charge carrier

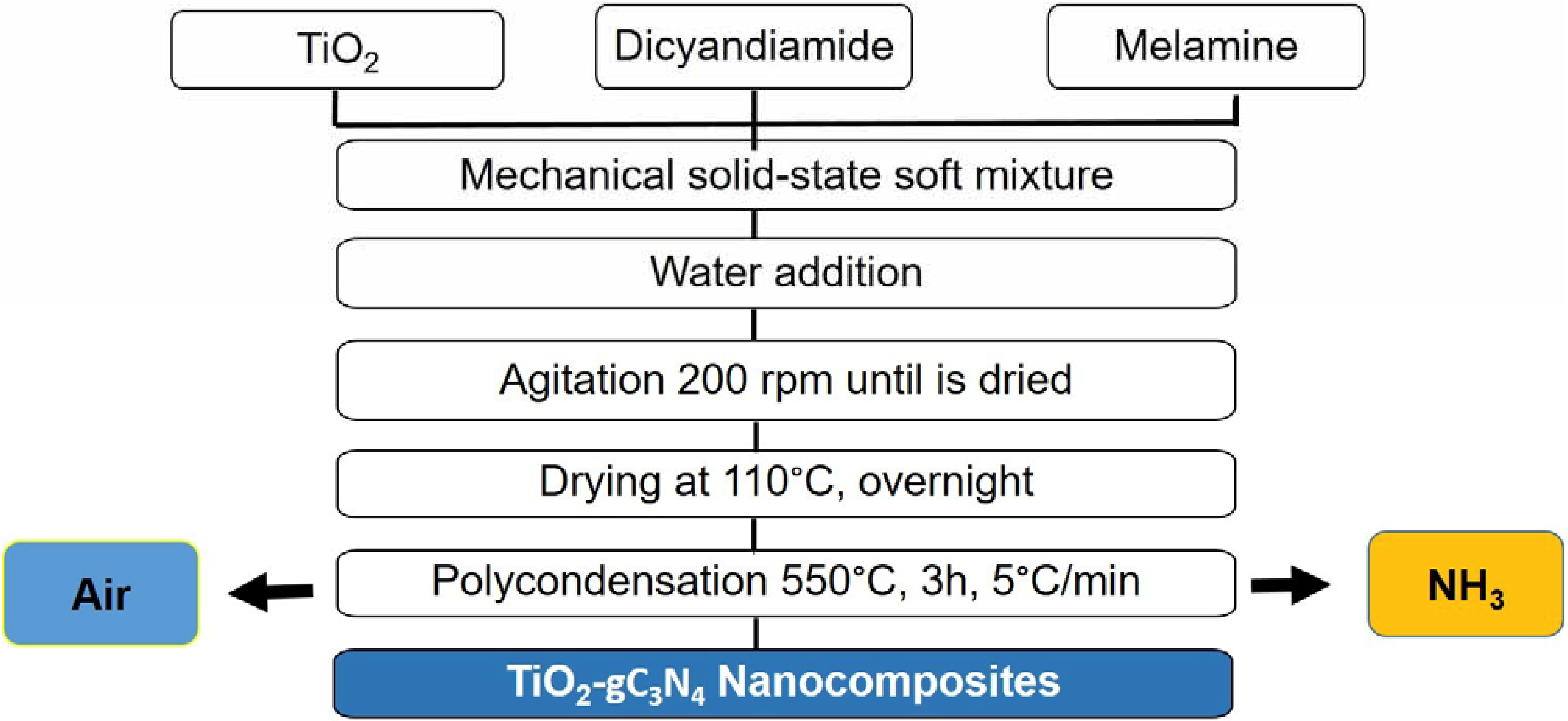
- Only the composite photogenerates charge dissociated carriers
- We assume that $g\text{-}C_3N_4$ generates e- and injects them from its CB to the TiO_2 CB

Kinetics of charge carriers TRMC results



- Same observations than at 450 nm excitation
  - But in a more attenuated way
- No generation of mobile electron carriers at 550 nm (maximum of Au NPs plasmon resonance)
  - No evidence of SPIE effect

➢Wet impregnation method



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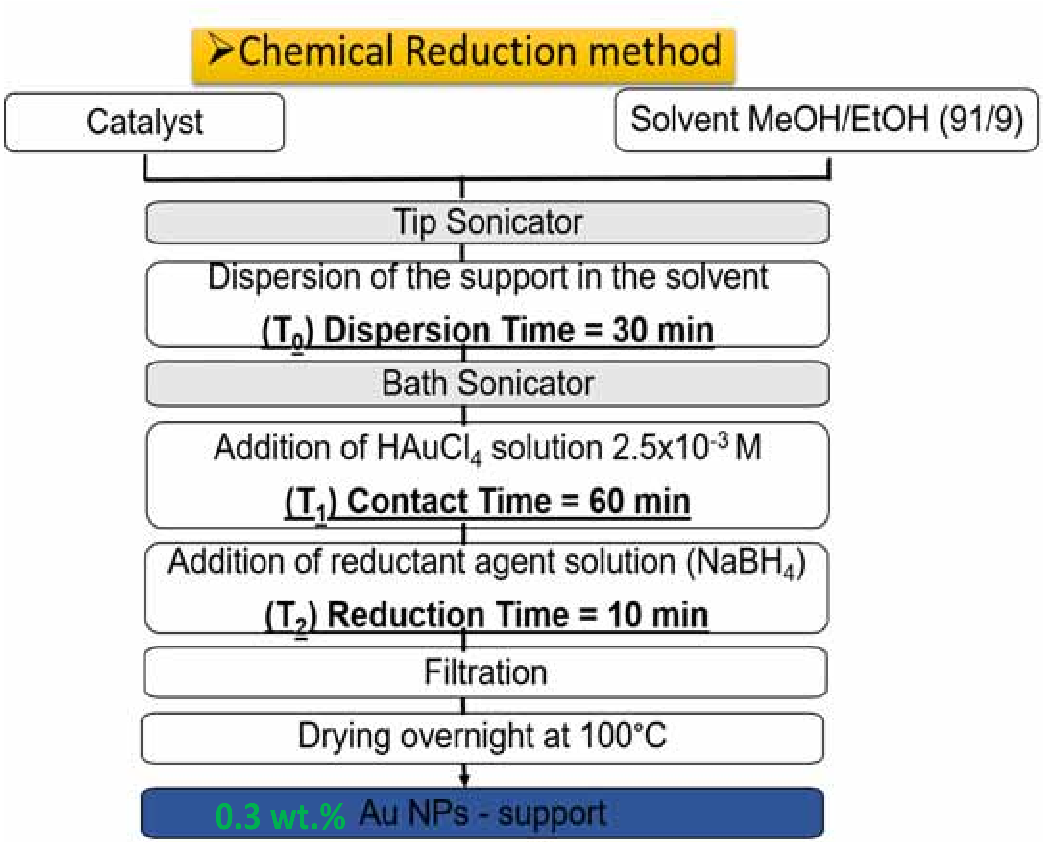
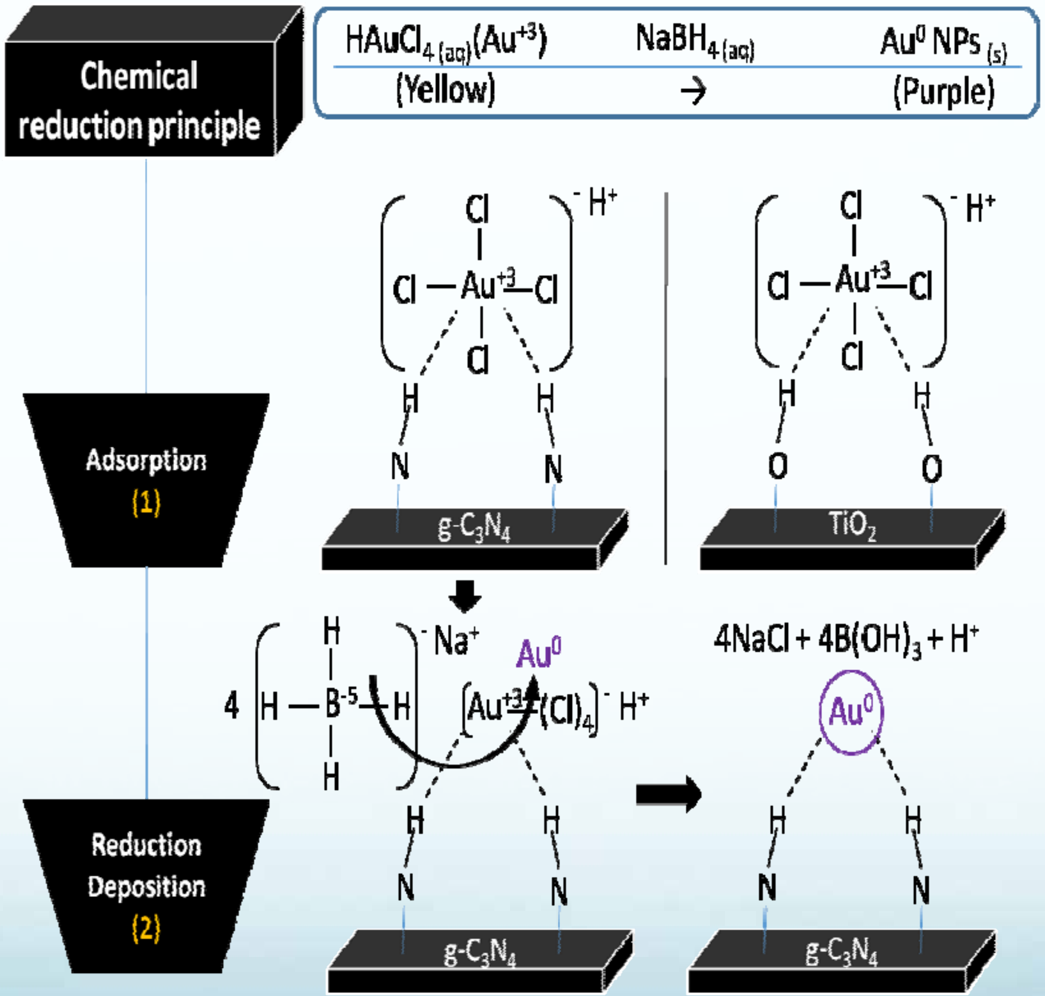
Noble metal / support deposition



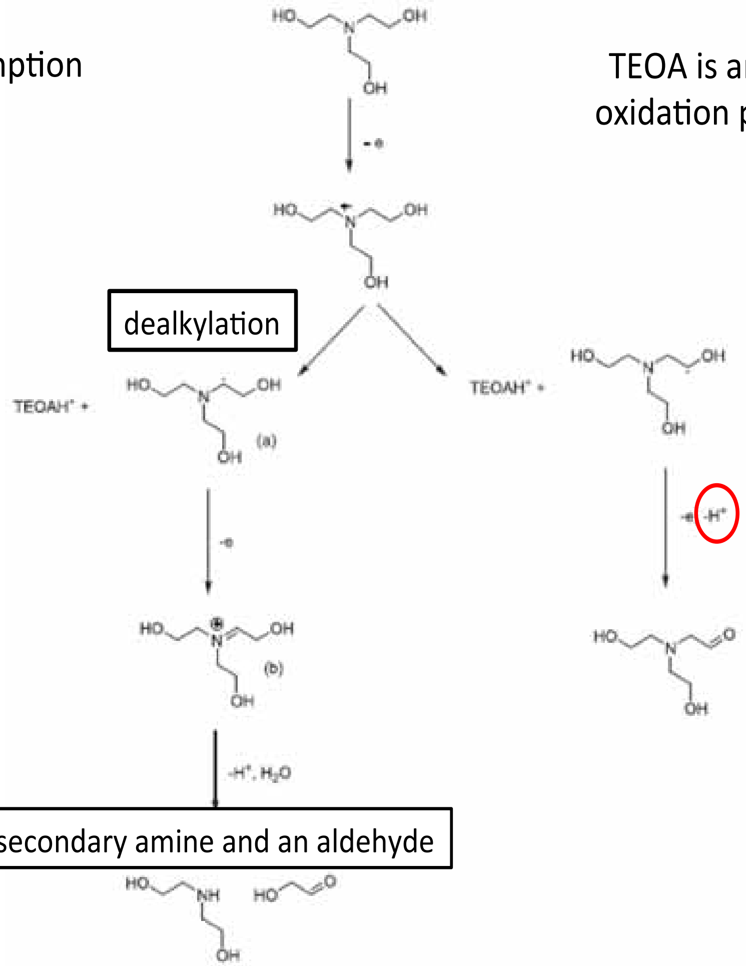
Scheme of Au NPs deposition mechanism principle



TEOA degradation (irreversible oxidation)

A hole scavenger or for O_2 consumption

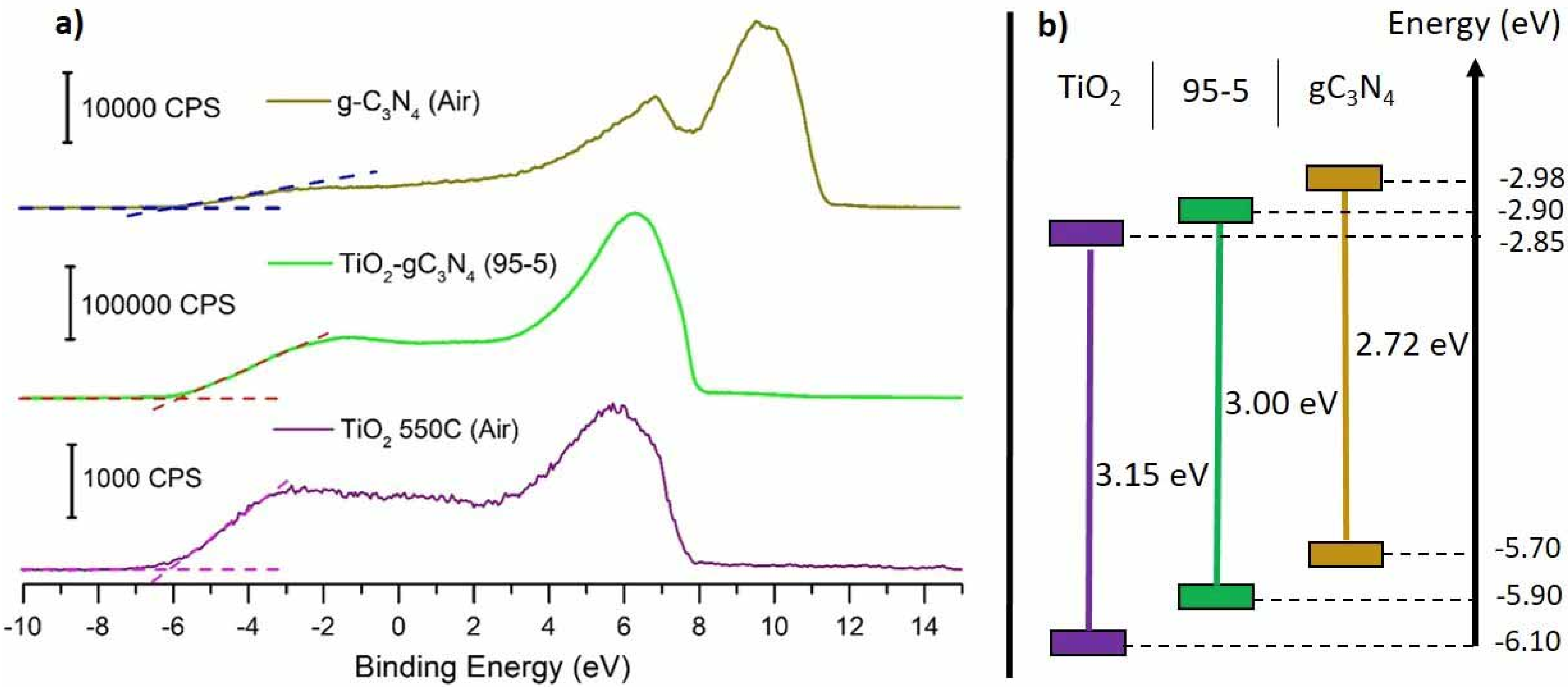
TEOA is an aliphatic tertiary amine with an oxidation potential of 0.6-0.7 *vs* NHE at pH 7



H^+ issued from TEOA degradation may also be implied in H_2 production mechanism in addition to water-splitting

Y. Pellegrin, F. Odobel, Sacrificial electron donor reagents for solar fuel production, Comptes Rendus Chim. (2016)

UPS results
Band edges positions



- ➢ Favorable heterojunction formation for enhanced charges separation and electrons injection
- ➢ New hybrid states

Surface plasmon benefits for photocatalysis

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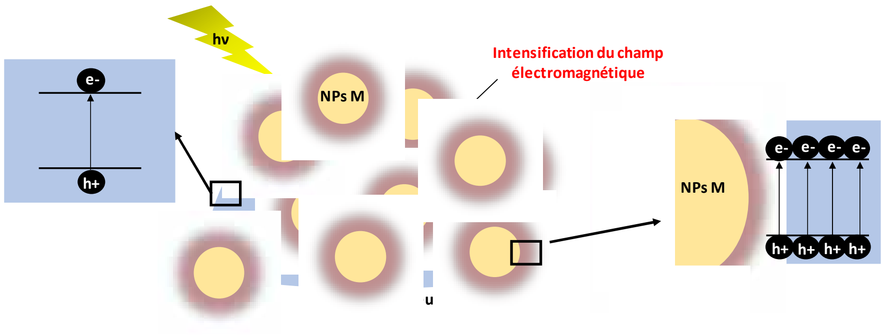
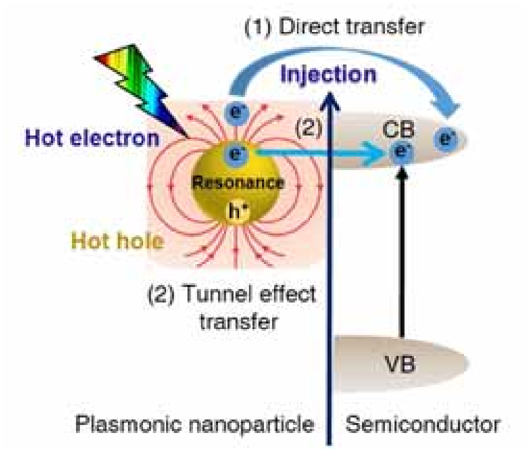
SC light absorption exaltation



Condition: For the electromagnetic field intensification in the surrounding of the M NP it has to have the same wavelength absorption than the SC (overlapping).

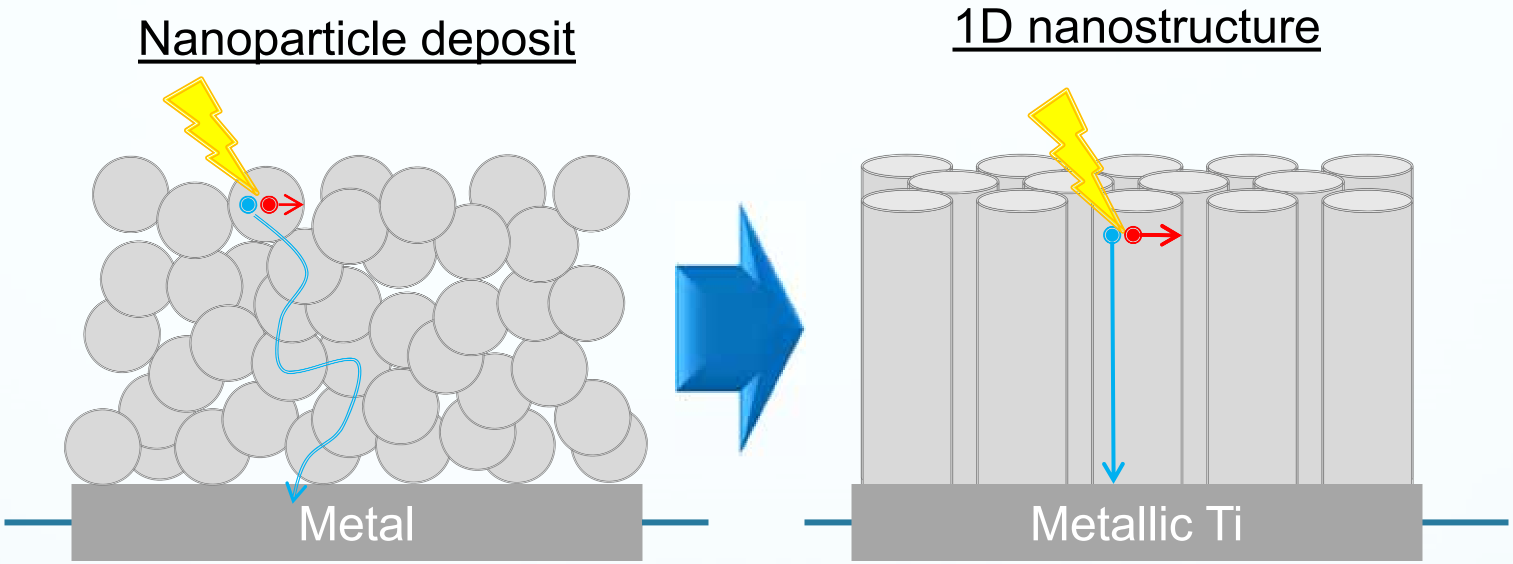
Hot electron injection



Note: The SC and M NP absorption do not need overlapped to allow the injection

TiO_2 photoanode

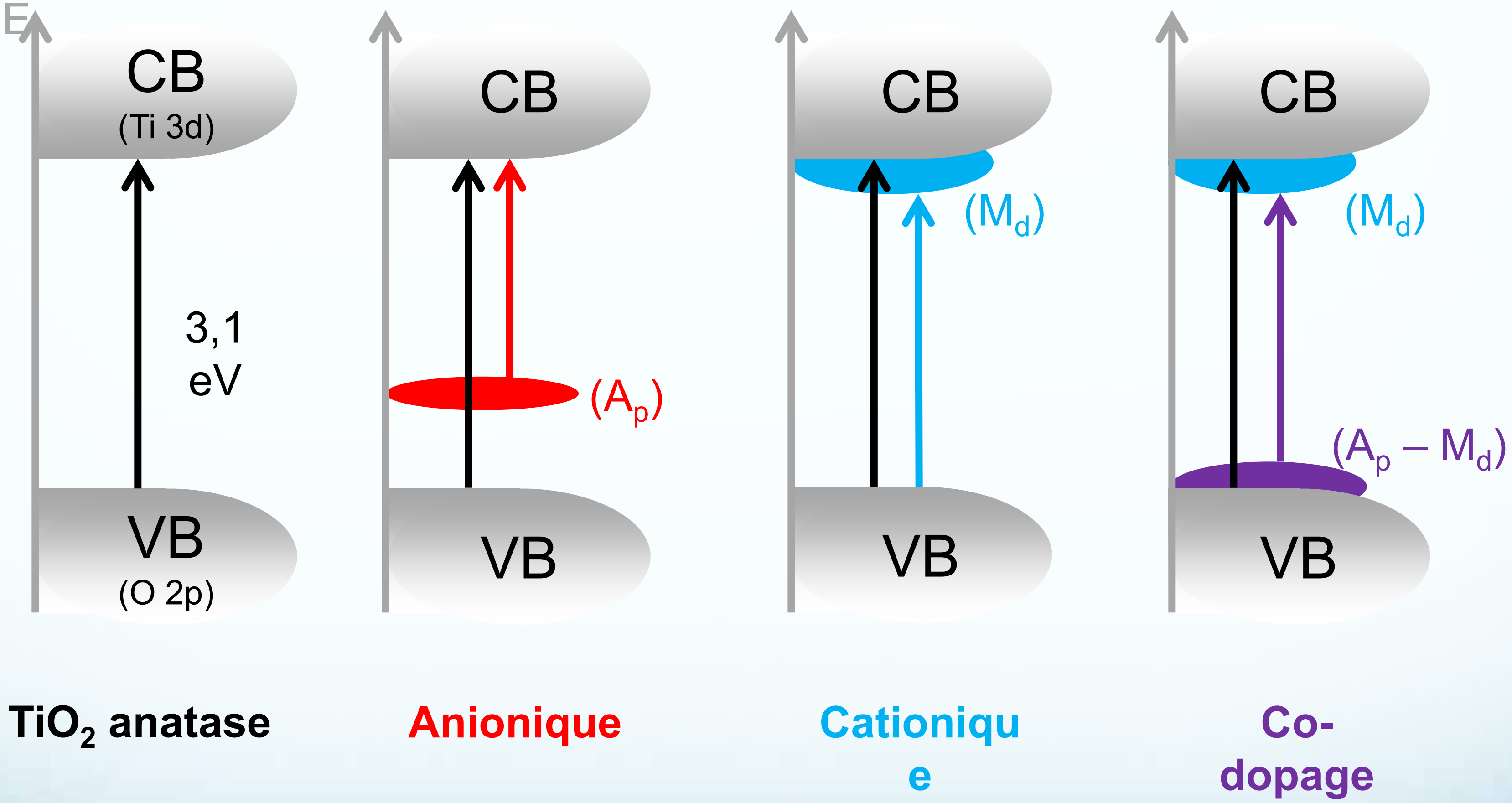
D. Gong, *et al.*, J. Mater. Res. 2001, 16, p3331



1 D nanostructure

- Unidirectional and separated paths for charge carriers
- Dimension in the order of the mean free path of minority charge carriers (holes in TiO_2)
  - Reduction of electron/hole recombination

Dopage et co-dopage du TiO_2



Etat local accepteur A_p

- Agit comme centre de recombinaison

Etat donneur M_d

- Hybridation M_d-$Ti3_d$

Etat hybride (A_p-M_d)

- Continuum
- Pas de recombinaison électron-trous

SUNRISE
Flagship Européen

GDR Solar Fuels

The French Solar Fuels Network

solarfuels.cnrs.fr

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50 research teams
> 110 principal investigators

1. Materials Chemistry & Nanosciences (V. Keller)
2. Molecular & Bioinspired Approaches (Vincent Artero)
3. Enzymatic systems (Christophe Leger)
4. Theoretical Approches & Modelling (Philippe Sautet/Tangui Le Bahers)
5. Advanced Characterization Methodologies (Winfried Leibl)
6. Chemical Engineering & System Integration (Jean-François Cornet)