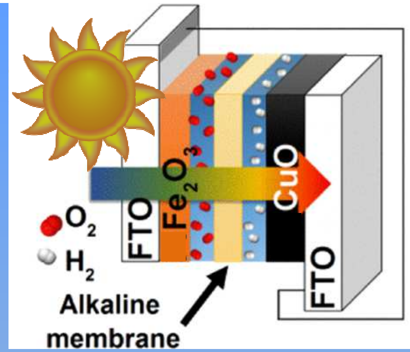
SP7

7th International Conference on Semiconductor Photochemistry

11-14 September 2019, Milano, Italy



DEVELOPMENT OF METAL OXIDE ELECTRODES FOR PHOTOELECTROCHEMICAL WATER SPLITTING TANDEM CELLS

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Comisión Europea

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FOTOH2 CONCEPT

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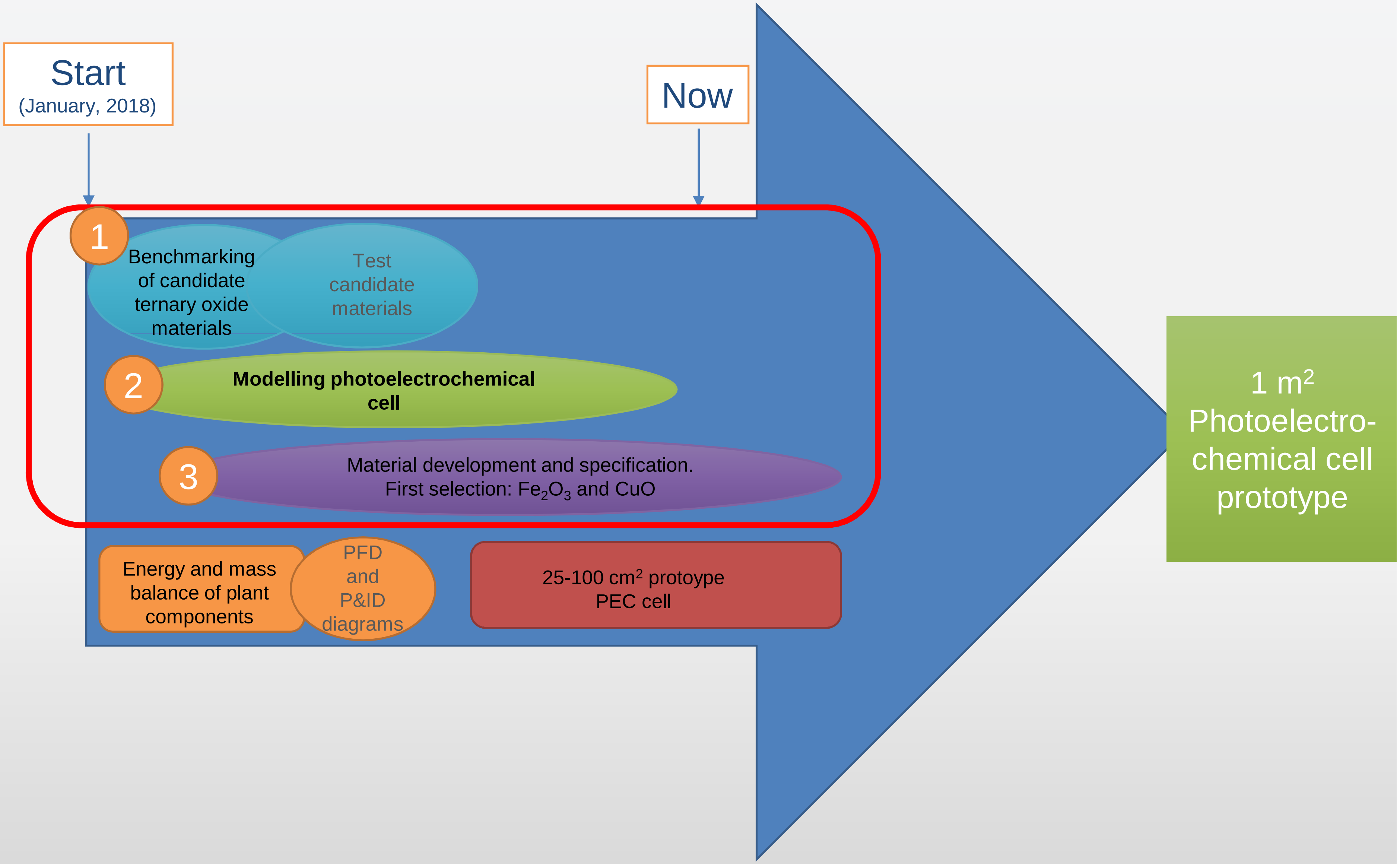
FotoH2 shall develop a **<u>highly efficient tandem photoelectrolysis</u>** cell for solar H2 production, based on **durable** and **cost-effective** advanced materials and interfaces. The following specific breakthroughs are targeted:

- Developing cost-effective advanced photoelectrode materials
- Achieving long-lasting cells for solar H_2 production
- Simple flow-cell design
- Production of pure H_2 in the output stream
- High Solar-to-Hydrogen conversion efficiency

FOTOH2 CONCEPT



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METHODOLOGY:

1. Bibliographic search: To know which materials were already well characterized (experimentally and theoretically) with consistent results from different research groups. The computational screening was applied to those materials with either no data or disagreeing data reported.

2. Screening methodology:

Density Functional Theory (DFT) based calculations

- Phase 1: Obtainment of reliable estimates of the **band gaps**. Those materials having either too low or too high band gap values were discarded.
- Phase 2: Evaluation of **transport properties** (carrier mobilities).

1. ELECTRONIC MODELLING – COMPUTATIONAL SCREENING

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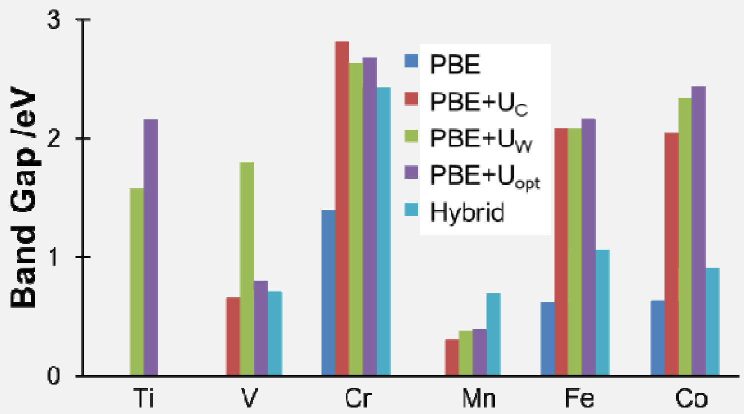
COMPUTATIONAL (DFT) SCREENED MATERIALS

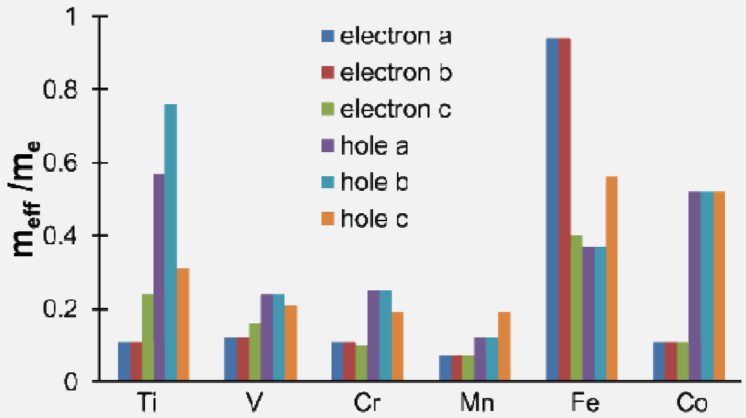
- **MgR_2O_4**
  R: Ti, V, Cr, Mn, Fe, Co — Mg-spinels
- **CaR_2O_4**
  R: Ti, V, Cr, Mn, Fe, Co — Ca-spinels
- **RAl_2O_4**
  R: Mg, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn — Al-spinels
- **RBi_2O_4**
  R: Mg, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) series — Bi-spinels
- **$R_xTi_yO_z$**
  R: V, Cr, Mn, Fe, Co, Ni, Cu, Zn) — Titanates

An example of computational screening: Mg spinels

Phase 1: band gap determination



Phase 2: carrier mobility determination

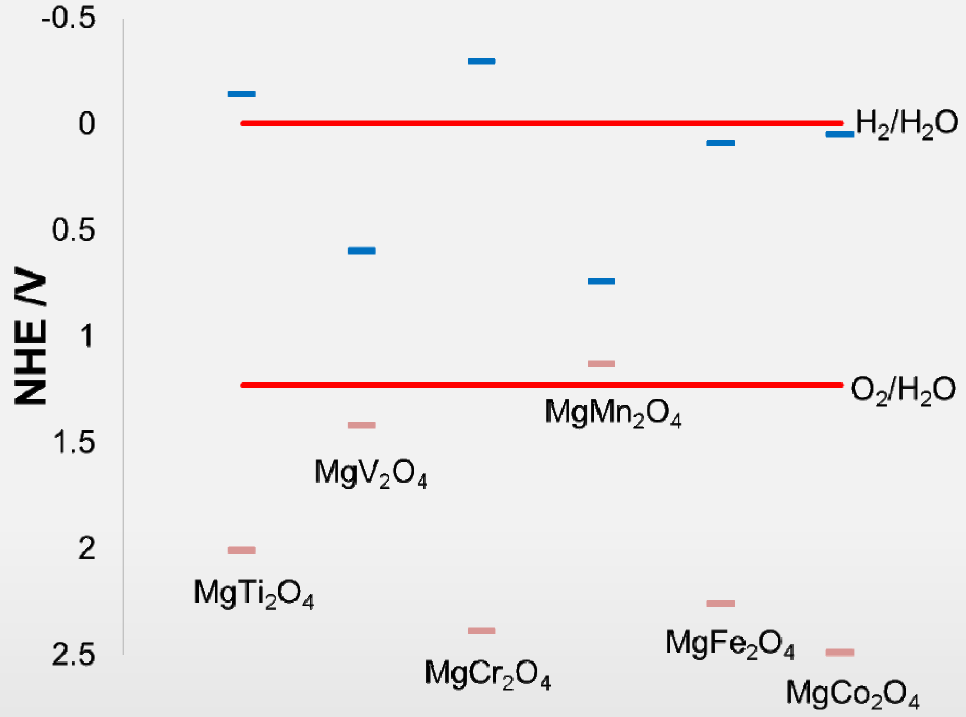


Not reported synthesis

$\tau=1\cdot10^{-15}$ s	electron μ /$cm^2\cdot V^{-1}\cdot s^{-1}$			hole μ /$cm^2\cdot V^{-1}\cdot s^{-1}$					
	a direction	b direction	c direction	a direction	b direction	c direction	Gap /eV	Gap type	Observations
$MgTi_2O_4$	15.98	15.98	7.43	3.06	2.31	5.74	2.15	I	OS rare and low mob.
MgV_2O_4	14.61	14.61	10.67	7.24	7.24	8.49	0.82	I	low mob.
$MgCr_2O_4$	16.73	16.73	17.92	7.05	7.05	9.11	2.68	D	Gap too high
* $MgMn_2O_4$	25.22	25.22	24.66	14.79	14.79	9.05	0.39	D	Gap too low
* $MgFe_2O_4$	1.87	1.87	4.43	4.81	4.81	3.12	2.17	I	low mob.
* $MgCo_2O_4$	16.67	16.67	16.67	3.37	3.37	3.37	2.44	I	low mob.

1. ELECTRONIC MODELLING – COMPUTATIONAL SCREENING

Band energy positions:



Allow to predict if the material is able to act as a photocathode or photoanode for water splitting

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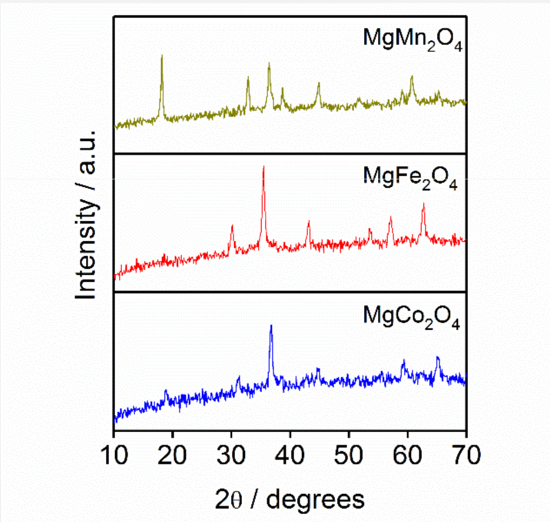
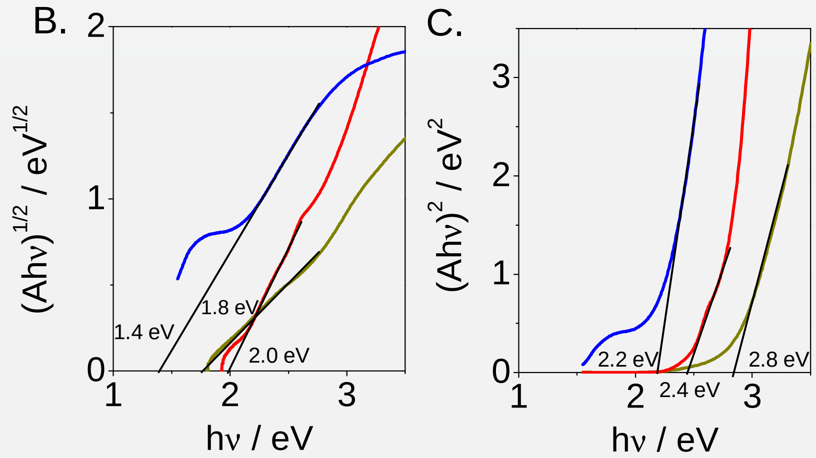
Benchmarking → Laboratory testing

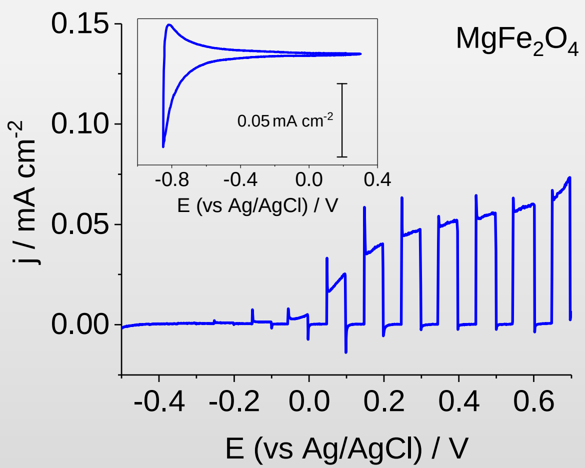
- X-ray difractogram



- UV-visible spectra: **TAUC PLOTS**



- Photoelectrochemical characterization



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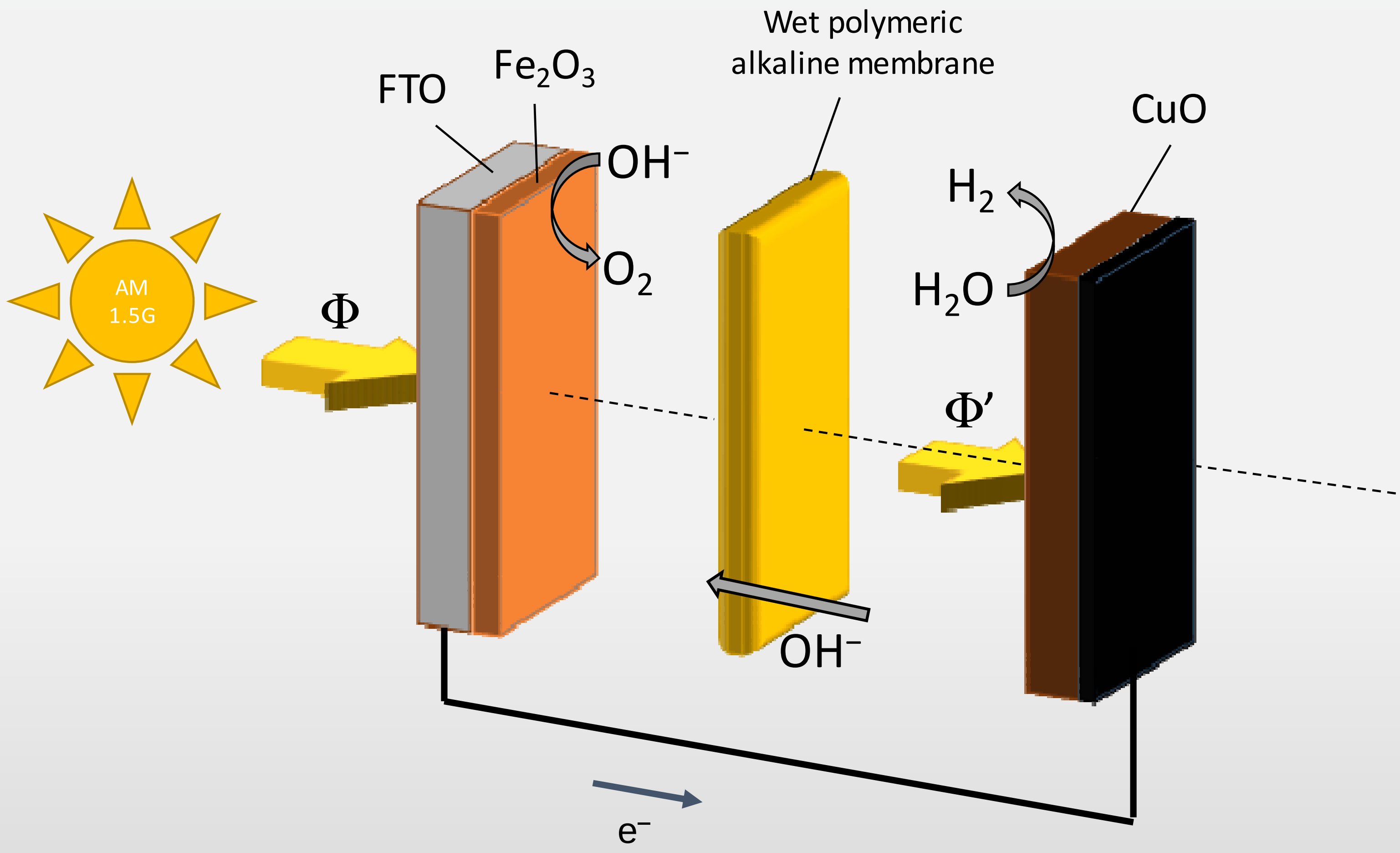
Analytical model based on FOTOH2 concept



2. ANALYTICAL MODEL

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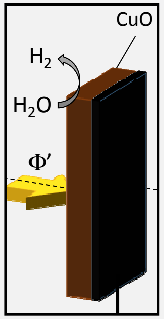
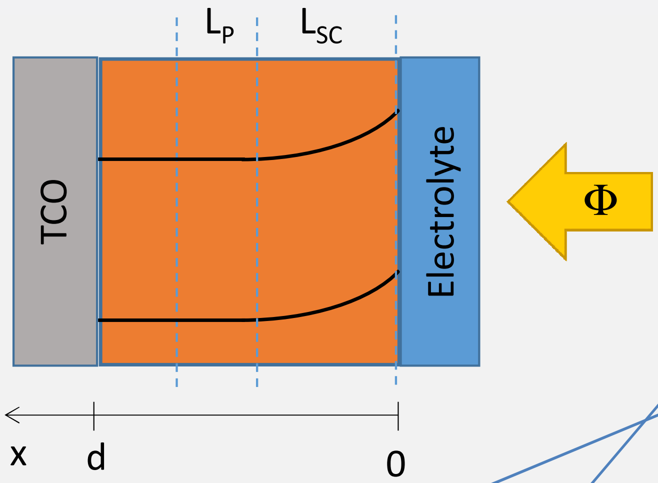
MODEL FOR **FRONT** ILLUMINATION (PHOTOCATHODE) → GÄRTNER MODEL





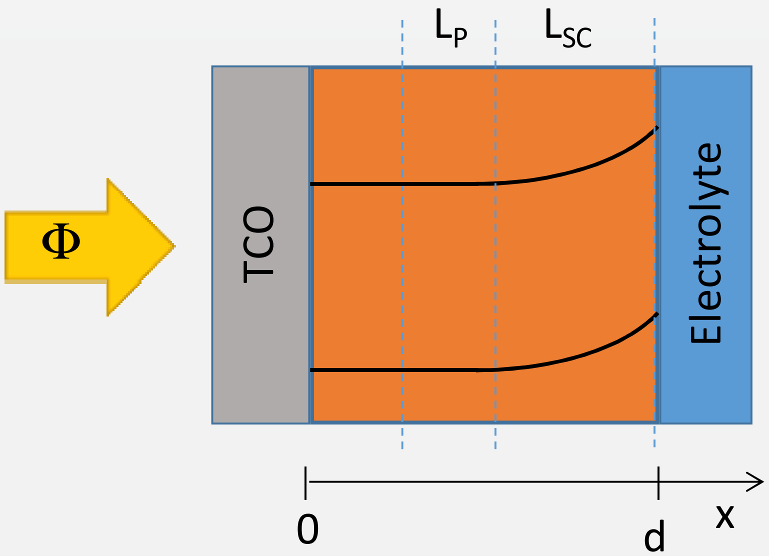
IMPROVEMENTS RESPECT TO THE ORIGINAL MODEL:

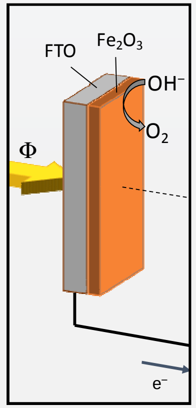
a) Polychromatic light: AM 1.5G (instead of monochromatic light)
b) Kinetic model (recombination and charge transfer rate constants)
c) Absorption coefficients as a function of the wavelength (Tauc relationships)

$$j_{ph,cat} = q\frac{k_{trans,cat}}{k_{trans,cat}+k_{rec,cat}}\int_{\lambda_{min}}^{\lambda_{max}} \Phi'(\lambda)\left(1-\frac{e^{-\alpha'(\lambda)L_{SC}^{cat}}}{1+\alpha'(\lambda)L_n}\right)d\lambda$$

2. ANALYTICAL MODEL

MODEL FOR **BACK** ILLUMINATION
(PHOTOCATHODE)





$$j_{TOT} = q\frac{k_{trans,an}}{k_{trans,an}+k_{rec,an}}\int_{\lambda_{min}}^{\lambda_{max}} \Phi(\lambda)\left[\left(1+\delta\left(1+\frac{\tanh\left(\frac{d-L_{SC}^{an}}{L_p}\right)}{\alpha(\lambda)\,L_p}\right)\right)e^{\alpha(\lambda)\left(dL_{SC}^{an}\right)}\left(\delta\ \mathrm{sech}\left(\frac{d-L_{SC}^{an}}{L_p}\right)+e^{-\alpha(\lambda)\,d}\right)\right]d\lambda$$

$$\text{where } \delta = \frac{(\alpha(\lambda)L_p)^2}{1-(\alpha(\lambda)L_p)^2}$$

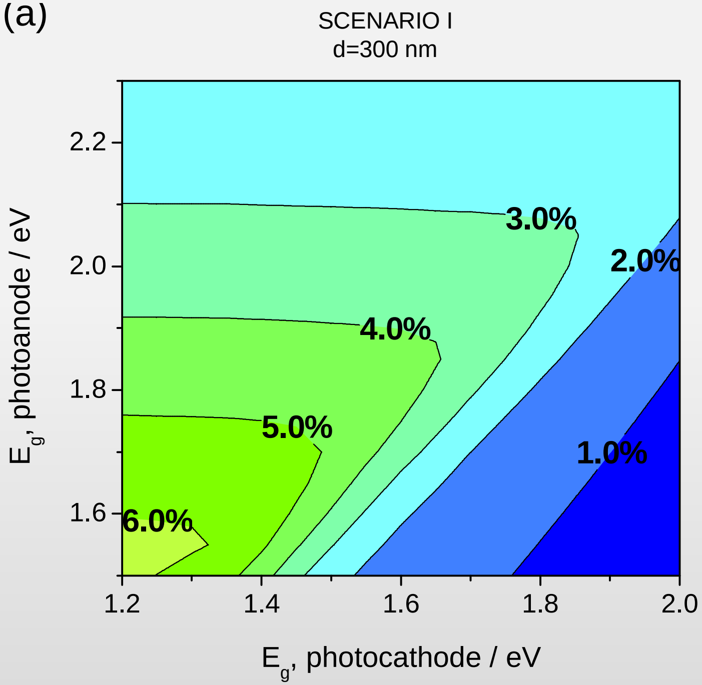
2. ANALYTICAL MODEL

PARAMETER	SCENARIO I	SCENARIO II
$E_{fb,cat}$ - $E_{fb,an}$	1 V	1.5 V
$\varepsilon_{an} = \varepsilon_{cat}$	100	100
$N_{D,an}=N_{D,cat}$	10^{18} cm^{-3}	10^{17} cm^{-3}
$L_{p,an} = L_{n,cat}$	50 nm	50 nm
β	1	1
k_{rec}^0/k_{trans}	10^4	10^4

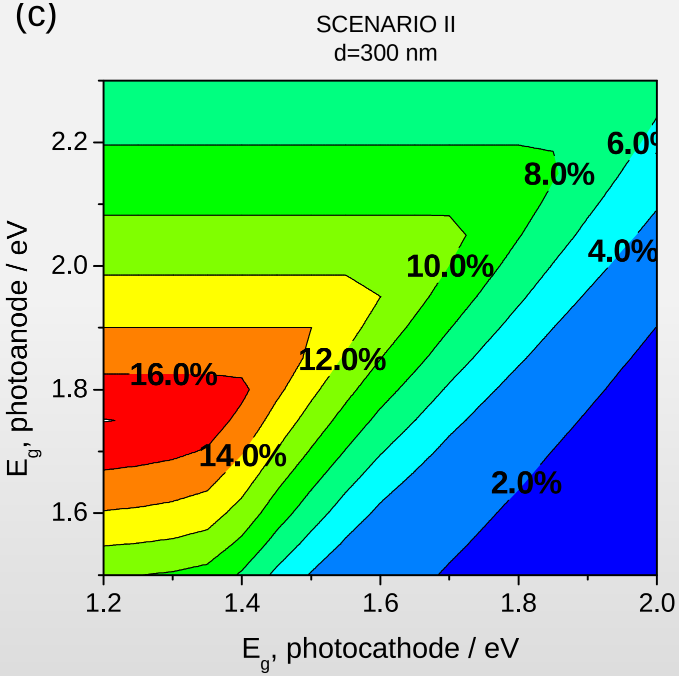
$$E_{cell} = E_{an} - E_{cat} + IR$$

$$STH(\%) = \frac{j_{ph}\, 1.23\ V}{P_W}\, 100$$

(a)



(c)



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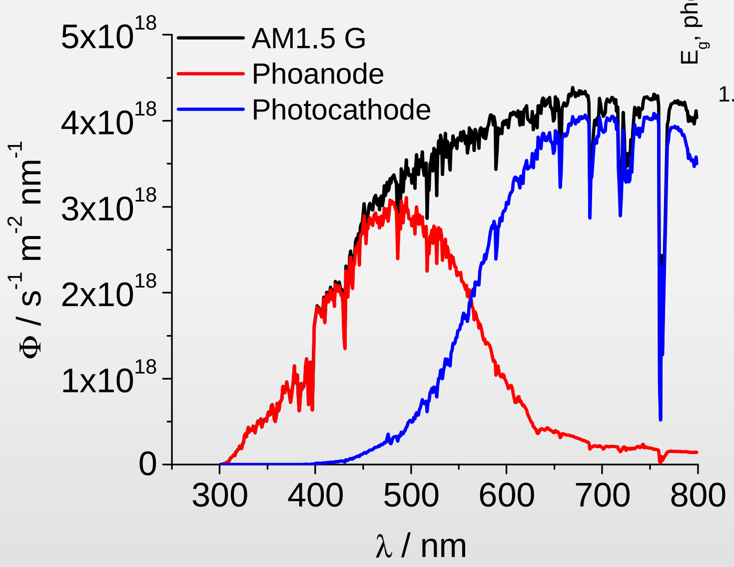
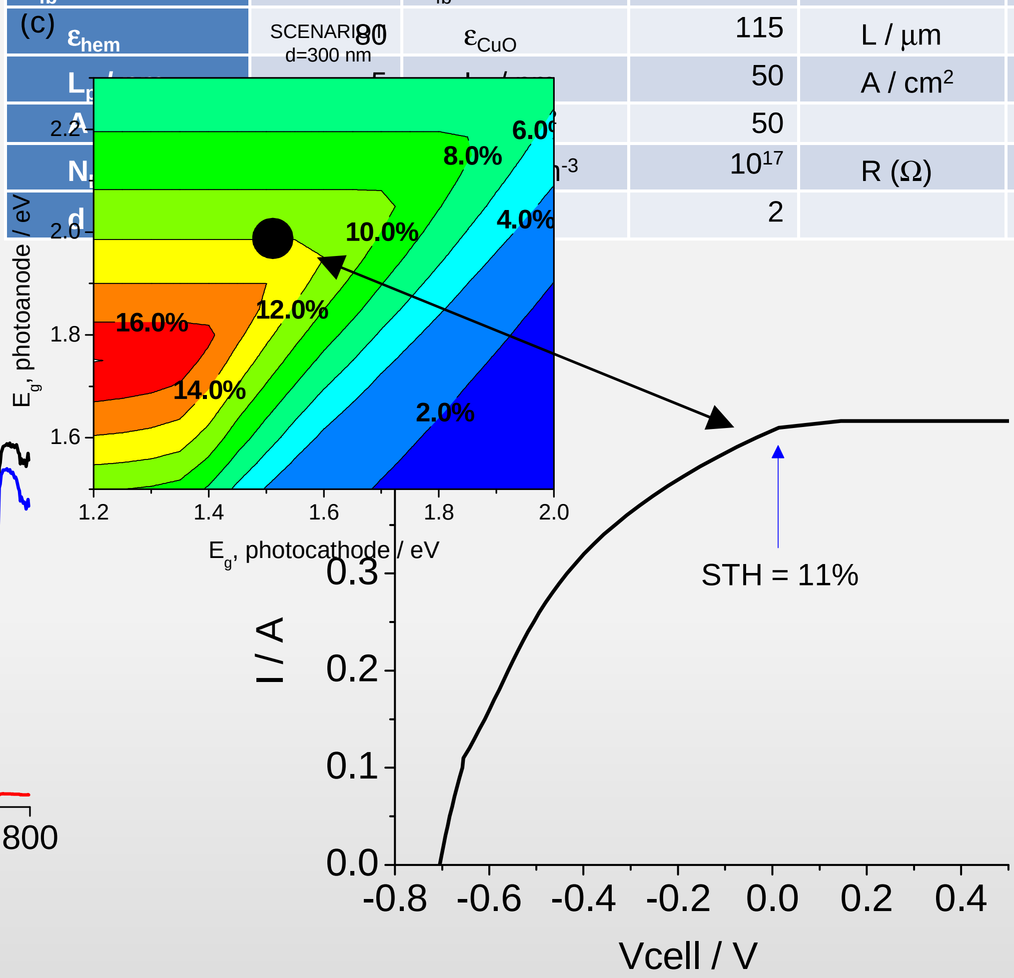
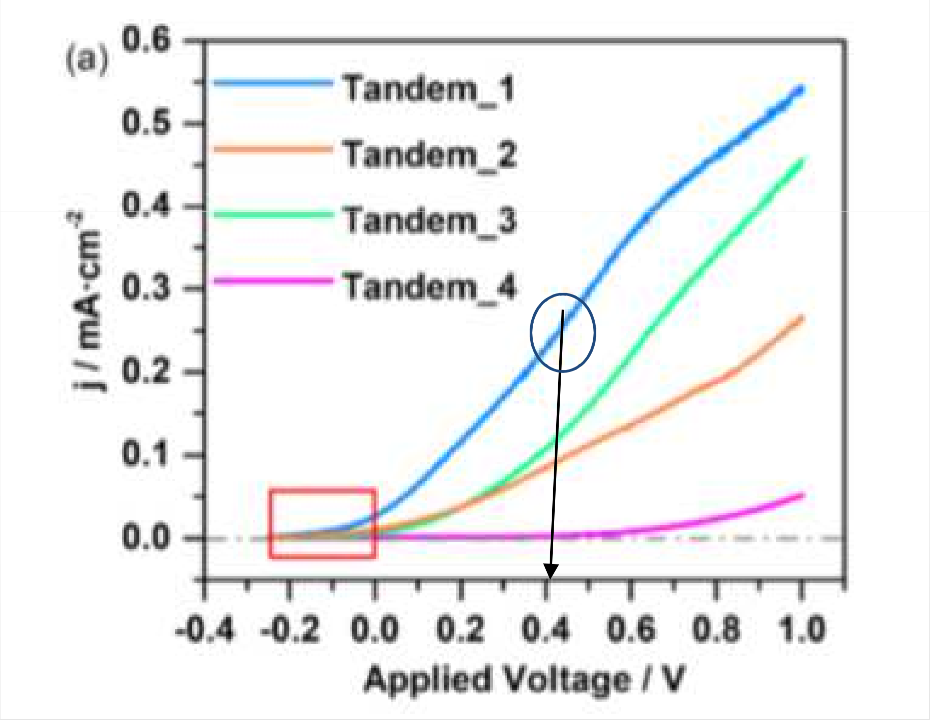
TANDEM CELL: HEMATITE-CuO

PHOTOANODE		PHOTOCATHODE		MEMBRANE	
E_{fb} / V vs RHE	0.3	E_{fb} / V vs RHE	1	σ / S cm^{-1}	0.1
ε_{hem}	80	ε_{CuO}	115	L / µm	50
L_p [illegible]	[illegible]	[illegible]	50	A / cm^2	50
A [illegible]	[illegible]	[illegible]	50		
N [illegible]	[illegible]	[illegible] cm^{-3}	10^{17}	R (Ω)	0.001
d [illegible]	[illegible]	[illegible]	2		





EXPERIMENTAL RESULTS ON Hematite-CuO PEM CELL



Optimization of the materials and interfaces
→ 1 mA/cm^2 at 0.4 V

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CONCLUSIONS

- Computational screening of materials based on DFT is a good approach for selecting the most promising metal oxide materials between a huge number of possibilities.

- Modelling polymeric electrolyte tandem cell by using a Gartner model-based approach allows to estimate reliable STH efficiencies in tandem cells based on the materials band gaps.

- Optimization of materials and interfaces in the polymeric electrolyte tandem cell allows to achieve reasonable efficiencies by applying an affordable value of applied bias.

FOTOH2 PROJECT: **http://fotoh2.eu**

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