COMPUTATIONAL SCREENING OF TERNARY SEMICONDUCTING OXIDES FOR DIRECT PHOTOELECTROCHEMICAL WATER SPLITTING

José Manuel Orts, Francisco José Pastor y Roberto Gómez
Universidad de Alicante

Krakow 14-19th May 2018

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 760930

FotoH2

Innovative Photoelectrochemical Cells for Solar Hydrogen Production

Acronym: FotoH2 Webpage:fotoh2.eu

Horizon 2020 Research & Innovation Programme - Grant number 760930

Consortium members:

- University of Alicante (coordinator)
- BroadBit Energy Technologies
- Consiglio Nazionale delle Ricerche (CNR-ITAE)
- HyGear
- ATS Solutions (ATS)

Goal: module of 1 m^2 photoelectrolyser with solar-to-H_2 efficiency of 10 %

Universitat d'Alacant
Universidad de Alicante

broadbit

Consiglio Nazionale delle Ricerche

ITAE

HYGEAR

ATS

FOTOH2

Tandem cell

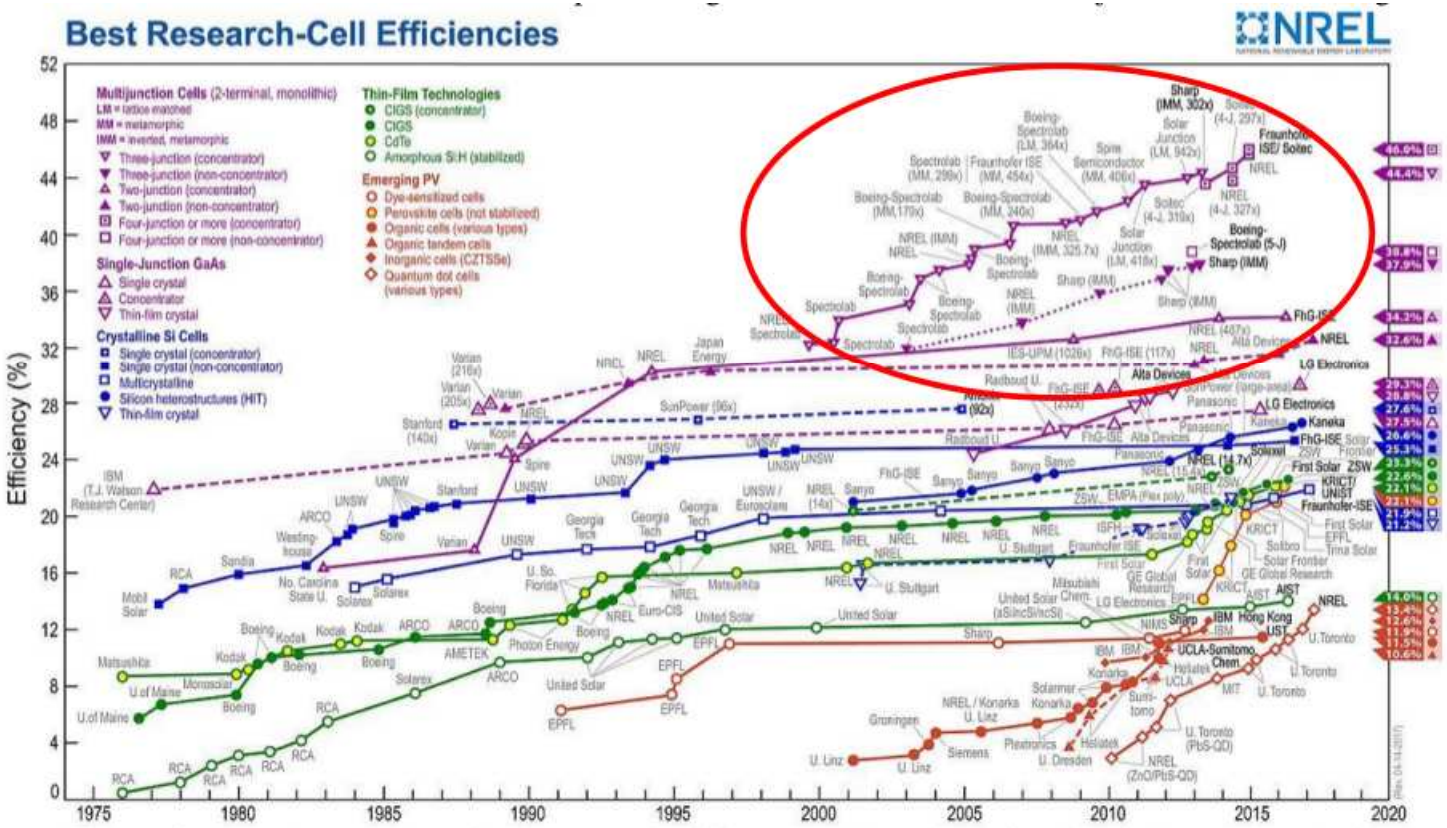


Figure 3: Historic evolution of solar PV cell efficiencies. The red circling highlights tandem device architectures, which are the highest performing (source: National Renewable Energies Lab, USA)

Tandem cell

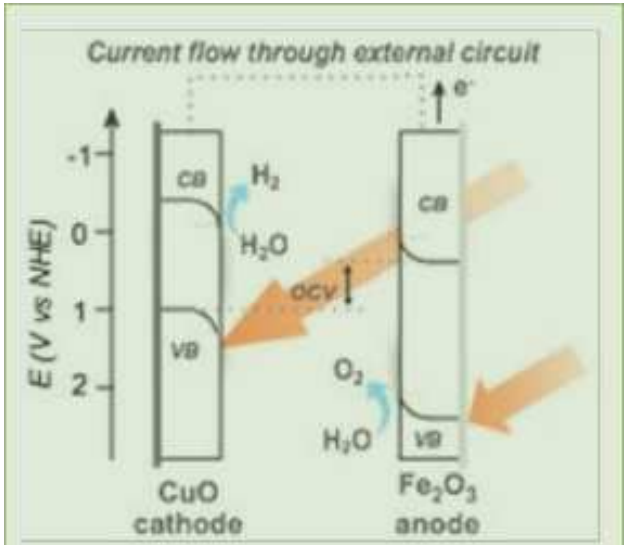


Figure 4: The operating principle of the planned hybrid tandem photoelectrochemical system

→Maximizes use of solar radiation

→ Initial materials choice:

α-Fe_2O_3 : n-type, Eg = 2.2 eV

CuO : p-type, Eg = 1.3 eV

→Search for alternatives: computational screening provides candidates for experimental benchmarking

Computational screening

- **Objective of computational screening :**
  - Search for earth-abundant ternary metal oxide materials that could be alternatives to those initially proposed as photoelectrodes

- Estimated number of possible ternary oxides: ~10^5

- **Preselection** → Different families of ternary oxides
  - ABO_2 - Delafossites
  - AB_2O_4 - Spinels (normal and inverse)
  - ABO_3 – Perovskites , ilmenites
  - ABO_4 – Scheelites, wolframites

Computational screening

- **Operational leitmotiv:**
  - Discard as soon as possible those materials that are not expected to fulfill requirements
  - Using the less computationally expensive methodology that allows to make that decision

- **Selection criteria** → optoelectronic properties
  - PRIMARY:
    - Band gap → magnitude and type (direct/indirect)
  - SECONDARY:
    - Effective masses (e / hole), mobilities
    - Absorption coefficients

Screening methodology

- **Level 0** → Bibliographic and database search
  - Bandgap, structures, synthetic procedures
  - If reported gap values agree → calculation not needed

- **Level 1** → Standard DFT calculations (bulk, 3D) - VASP
  - PBE functional (Generalized Gradient Approximation)
  - PAW (plane wave formalism for periodic boundary)
  - DOS/Bands for experimental/optimized geometries.
  - Significantly underestimates bandgap.
  - Provides a lower bound for the real bandgap value.
  - Allows for rejection of unfavorable cases.

DFT + U approach

- **Level 2 → GGA + U (VASP)**
- Pure DFT → Kohn-Sham orbitals → 1-electron approach.
- Strongly correlated d and f electrons not adequately described
- DFT+U adds an effective correction term (no additional comput. cost)
- Hubbard-like hamiltonian (depends on orbital occupations)
- Significantly improves bandgap values
- Dudarev's method (one-parameter)
- Different published U values for a given metal and oxidation state
- U values usually adjusted to reproduce property of interest (band gap, oxide formation termochemistry, …)

U value

- "A high-throughput infrastructure for density functional calculations". A. Jain, G. Hautier, C.J. Moore, S.P. Ong, C.C. Fischer, T. Mueller, K.A. Persson, G. Ceder. Comp. Mater. Sci. 50 (2011) 2295.

  → fits U to match experimental formation enthalpies of binary oxides.

- "Local enviroment dependent GGA+U method for accurate thermochemistry of transition metal compounds". M. Aykol, C. Wolverton, PRB 90 (2014) 115105.

  → also fits U from formation enthalpies, distinguishes metal oxidation state and type of compound (oxides, hydroxides, …).

	U(ceder) /eV	U(wolv) /eV
Mg	0*	0*
Ca	0*	0*
Ti	0	4.35
V	3.1	4.86
Cr	3.5	3.04
Mn	3.9	4.54
Fe	4	4
Co	3.4	4.26
Ni	6	6.07
Cu	4	-
Zn	-	-

Hybrid functionals

- **Level 3** → Hybrid DFT calculations - VASP
  - HSE06 functional
  - Adds a fraction of Fock exchange.
  - Calculated band gap very close to experimental value.
  - Much more costly (10 to 50 times) than PBE.
  - Convergence more problematic
  - GPU memory limitations
  - Band structure → dielectric function, extinction coeff., …

Results

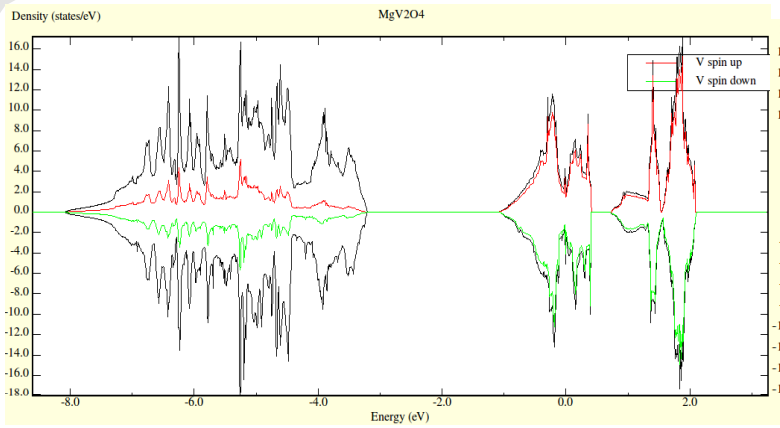
- **$LnCrO_3$. Lanthanide Chromium Perovskites.**
  - Level 0 discards : data exist / radioactive / expensive
  - Level 1: Pr, Nd, Sm, Eu, Gd, Tb, Er, Tm, Yb
  - PBE Bandgaps: 1.34-1.41 eV; 0.87 eV (Nd)
  - Bad description of electronic structure.
  - Needs explicit treatment of f-electrons (as valence)
  - Nonlinear magnetic systems.

Results

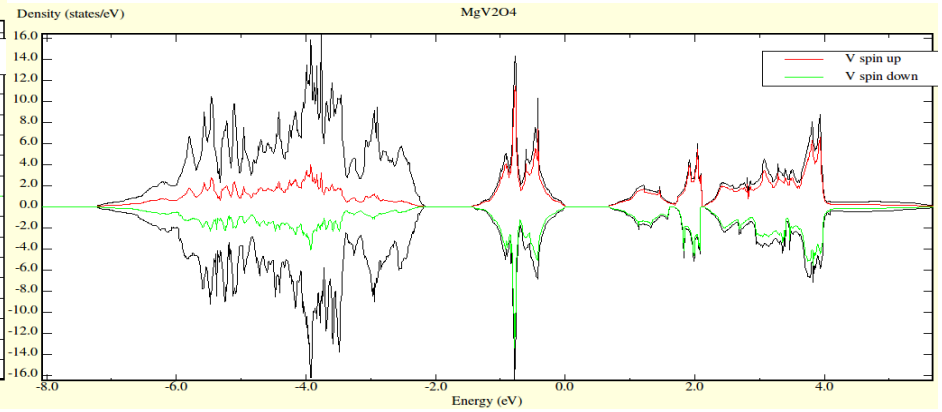
- **MgB_2O_4. Magnesium – transition metal normal spinels**
  - Level 0 discards: if not stable (databases)
  - Level 1: Ti, V, Cr, Mn, Fe, Co
  - → $MgCr_2O_4$: 1.7 eV experim.
  - → $MgCo_2O_4$: no published data

	gap /eV (opt a)		gap /eV (opt no U)		gap /eV (opt U Ceder)		gap /eV (opt U Wolv)	
$MgTi_2O_4$	-		metal		metal		1.60	
MgV_2O_4	metal		metal		0.68		1.94	
$MgCr_2O_4$	1.4		1.4		2.78		2.86	
$MgMn_2O_4$	metal		metal		0.33		0.37	
$MgFe_2O_4$-n	0.13		-		-		-	
$MgFe_2O_4$-I	0.24	up: 0.80	0.30	up: 0.85	2.10	up: 2.20	2.10	up: 2.20
		down: 0.60		down: 0.70		down: 2.80		down: 2.80
$MgCo_2O_4$	0.72		0.65		2.00		2.30	

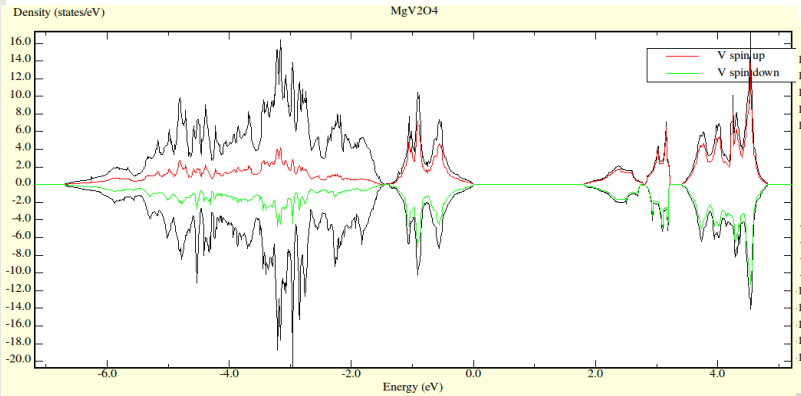
DOS → Eg



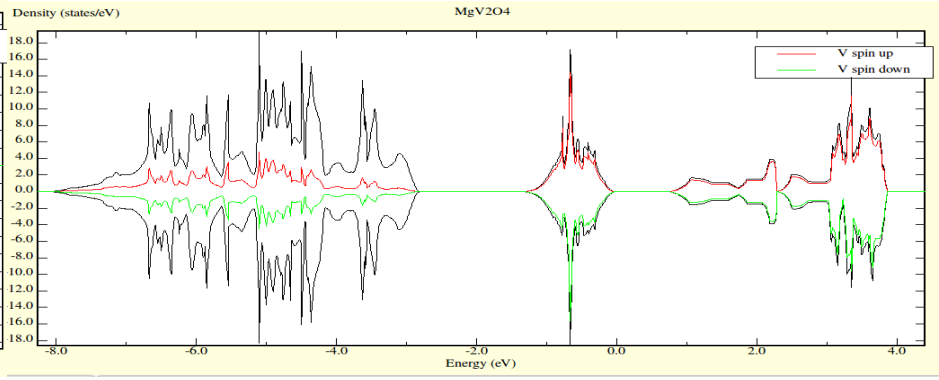
PBE



U = 3.1 eV; Eg = 0.68 eV

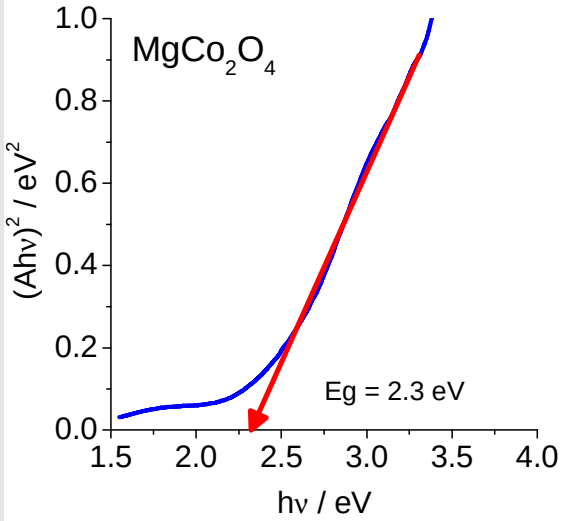


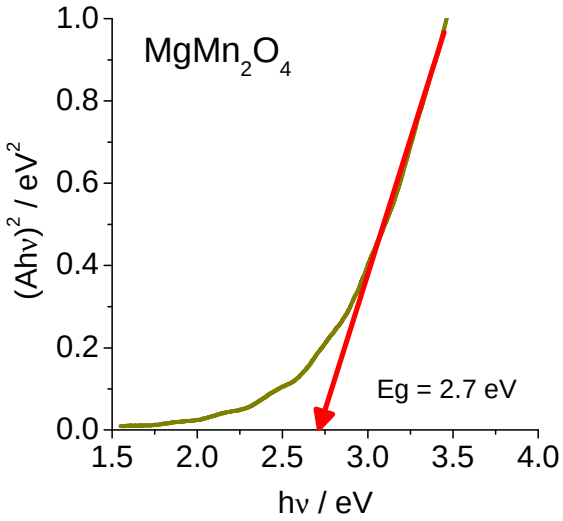
U = 4.86 eV; Eg = 1.94 eV

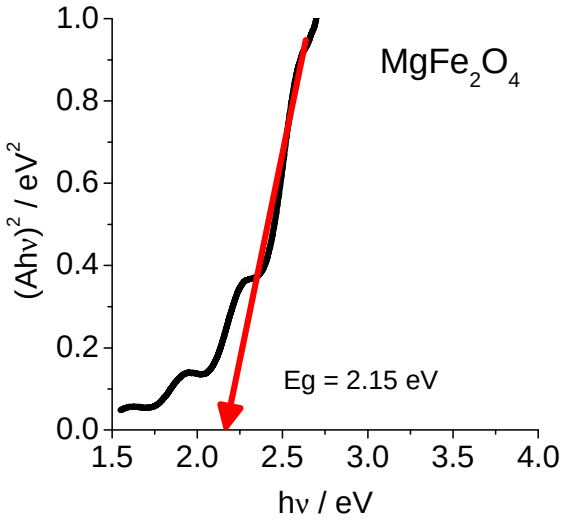


HSE06 (15%); Eg = 0.74 eV

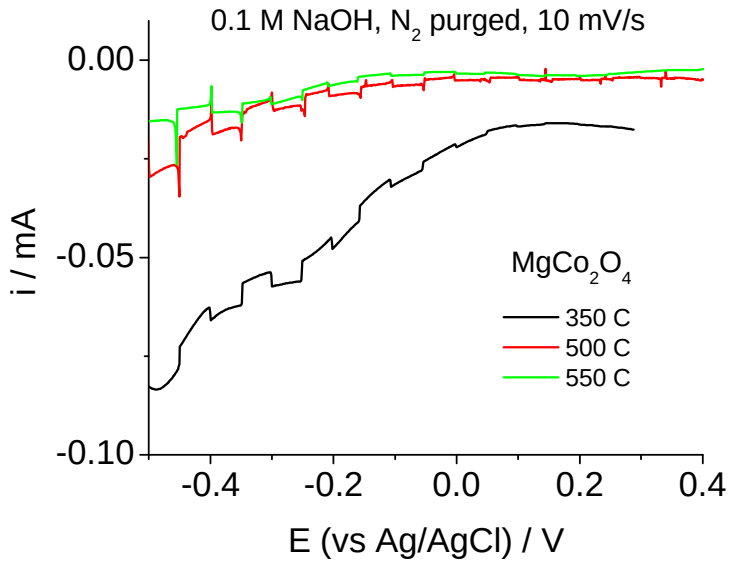
UV-vis TAUC PLOTS (direct band gap)

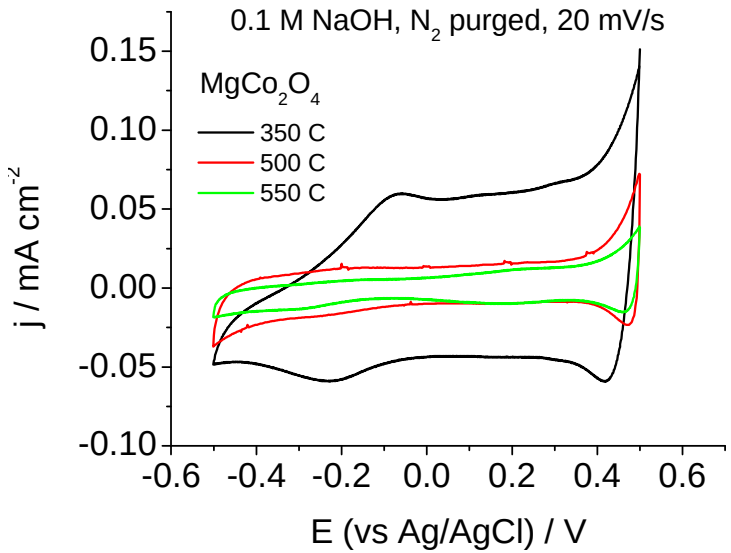




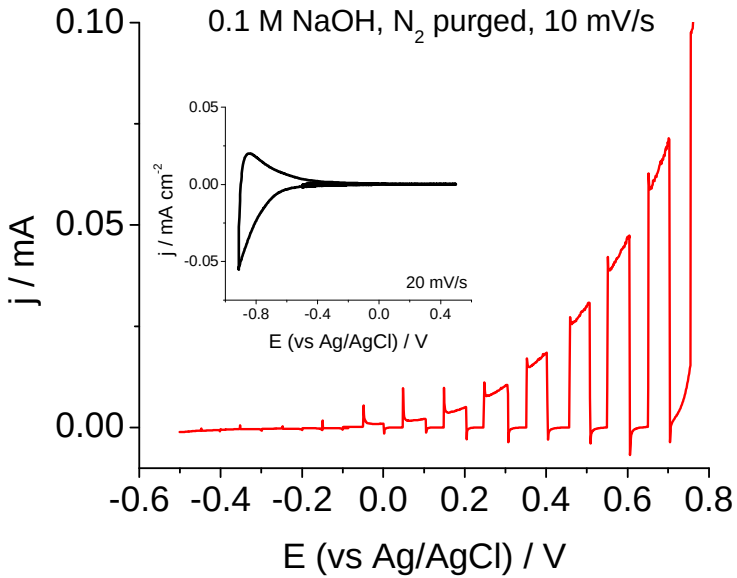


PEC – $MgCo_2O_4$


0.1 M NaOH, N2 purged, 10 mV/s
0.00
-0.05
-0.10
i / mA
-0.4
-0.2
0.0
0.2
0.4
E (vs Ag/AgCl) / V
MgCo2O4
350 C
500 C
550 C


0.1 M NaOH, N2 purged, 20 mV/s
0.15
0.10
0.05
0.00
-0.05
-0.10
j / mA cm-2
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
E (vs Ag/AgCl) / V
MgCo2O4
350 C
500 C
550 C

PEC – $MgFe_2O_4$ – 550 ºC



Material	Band gap (direct) / eV	Type	Onset / V vs RHE	Max Iph (≈1 cm^2)
$MgCo_2O_4$	2.3	P-	1.25	5 µA
$MgMn_2O_4$	2.7	P-	1.05	20 µA
$MgFe_2O_4$	2.15	N-	0.75-0.95	70 µA

Conclusions

Computational screening usin DFT can help in selecting potential ternary oxide candidates with a given range of Eg, to be used as photoelectrodes.

But remember:

- Perfectly ordered, infinite 3D system used for calculation.
- Surface states, structural defects, dopants, …. can significantly affect the electronic properties, and photoelectrochemical activities.
- P- or n- type to be tested experimentally.
- Hybrid functionals and many-body approaches give much better results than GGA+U, but at a much higher computational cost.

Acknowledgents

Funding:

Project FotoH2
Innovative Photoelectrochemical Cells for Solar Hydrogen Production
EC - Horizon 2020 Research & Innovation Programme - R&I Action – Grant 760930

Universitat d'Alacant
Universidad de Alicante

broadbit

HYGEAR

Consiglio Nazionale delle Ricerche

ITAE

ATS

Thank you very much for your attention !!

FOTOH2

THANK YOU FOR YOUR ATTENTION

Dr. José Manuel Orts
University of Alicante
Email: JM.Orts@ua.es
Phone: (+34) 965 90 98 09

This project has received funding from the European Union's Horizon2020 Framework Programme for research, technological development and demonstration under grant agreement no 760930