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(1RST MAY 2022 – EXPECTED END DATE : SEPTEMBER 2025, EXTENSION OF 5 MONTHS)

LEAP-RE

Long-Term Joint EU-AU Research and Innovation Partnership on Renewable Energy

Pillar-1 project

The LEAP-RE project has received funding from the European Union's Horizon 2020 Research and Innovation Program under Grant Agreement 963530.

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Consortium

Project coordinator:

- Raphaël Schneider, Université de Lorraine, **France**

Project partners:

- University of Liege (**Belgium**),
- Université de Lorraine (**France**),
- Mohammed V University in Rabat (**Morocco**),
- Mohammed VI Polytechnic University (**Morocco**)
- University of the Witwatersrand (**South Africa**)

Aim of the project

- Develop new QDSSCs using heavy metal-free QDs as absorbing material in the visible and infrared regions for optimal use of the solar spectrum.
- Optimize the interface between Cu-In-Zn-Se or $CsSnX_{3-x}Y_x$ QDs and the TiO_2 photoelectrode using wet and vacuum deposition processes.

Relevance vs MARs

- Find new materials and better design PV cells to **make more efficient solar panels and decrease their cost for generating clean and renewable electricity**.
- Develop devices that will **allow not only autonomous but also decarbonated production of electricity and thus ensure energy independence.**

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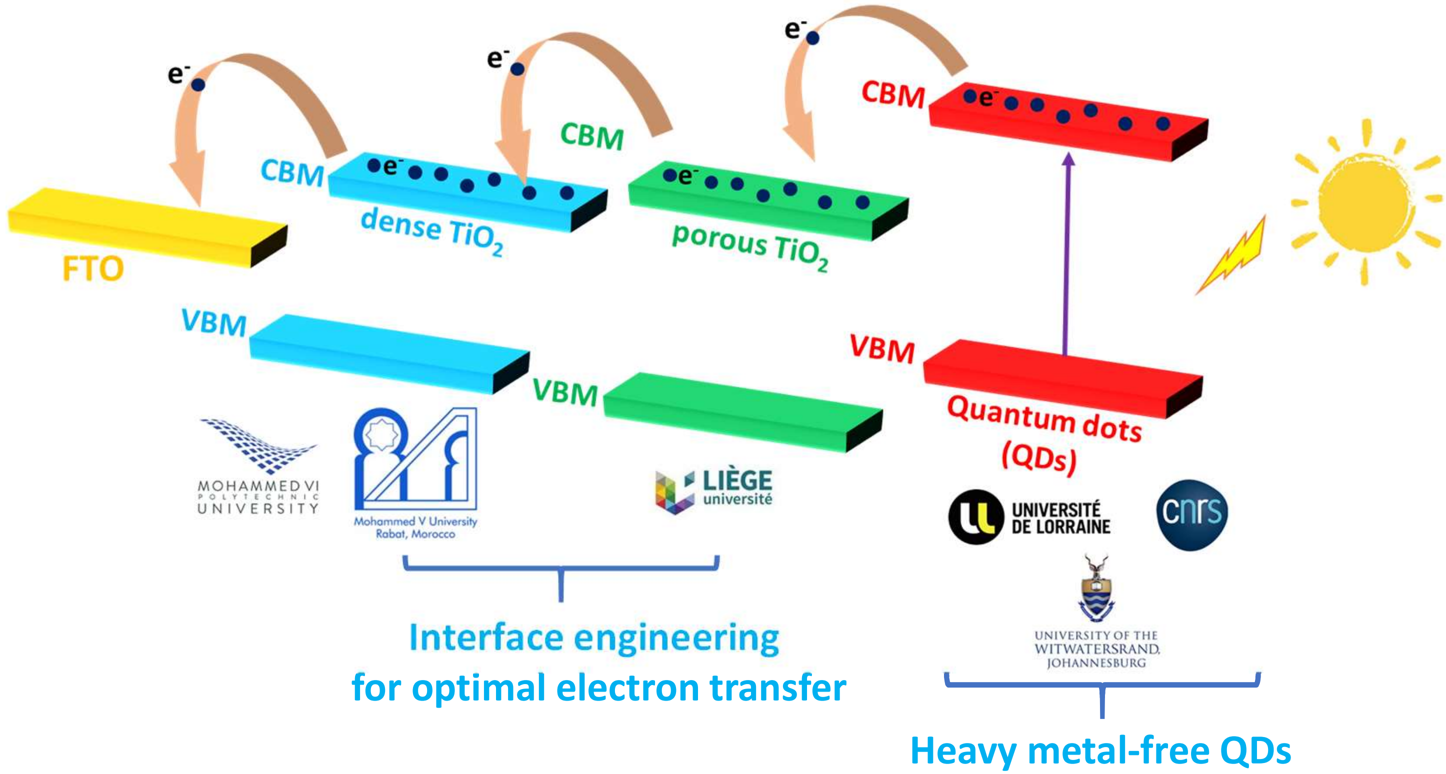
Quantum dots-sensitized solar cells



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Key challenges addressed by the project

1. Develop new syntheses of heavy metal-free Cu-In-Zn-Se and $CsSnX_{3-x}Y_x$ and or doped $CsSnX_3$ QDs with optimal electronic and optical properties for use in QDSSCs.
2. Optimize the structure and the electronic properties of the dense TiO_2 layer via magnetron sputtering and of the porous TiO_2 layer by wet-based templating strategies.
3. Control the microstructure of the TiO_2 porous network, in order to form continuous and highly condensed interpenetrating nanochannels allowing to maximize QDs to TiO_2 charge injection and minimize recombination.
4. Establish the excited state and charge transfer properties of Ag-In-Zn-Se and $CsSnX_{3-x}Y_x$, as well as their interaction with TiO_2 to further boost the QDSSCs efficiency.

Expected results

- Achieve **power conversion efficiencies (PCEs) above 15%,** which constitutes a ground-breaking challenge for heavy metal-free PV cells.

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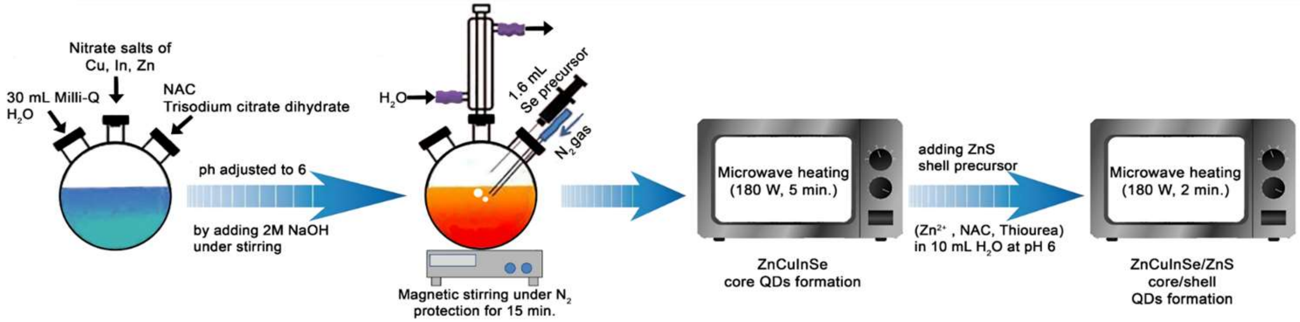
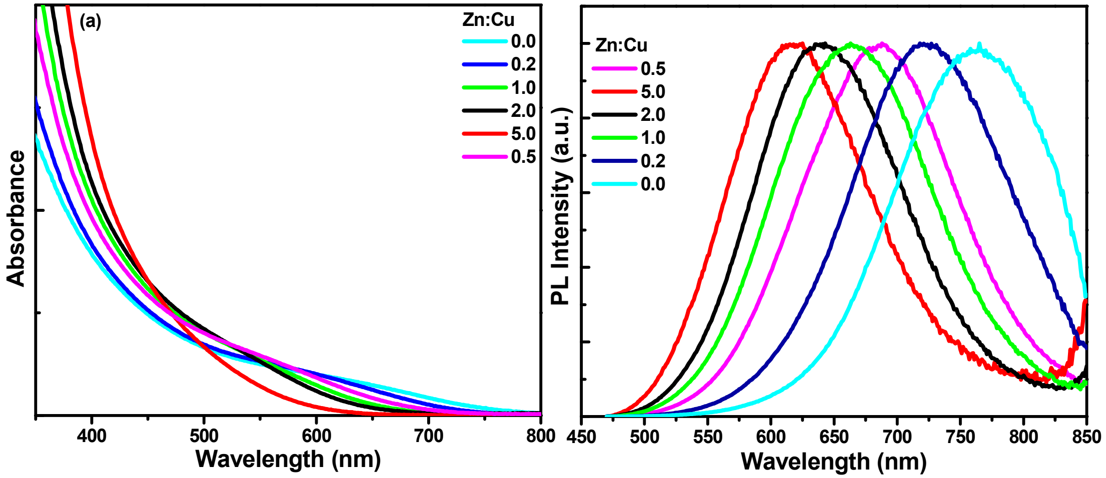
WP1 : Synthesis & optimization of Cu-In-Zn-Se/ZnS QDs – Université de Lorraine and CNRS

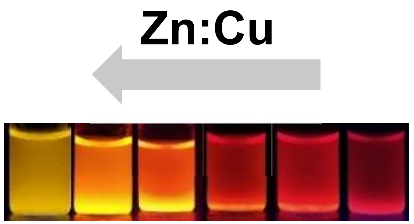
New microwave assisted-aqueous phase method to produce Cu-In-Zn-Se QDs

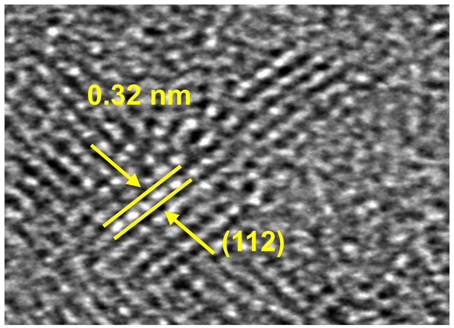


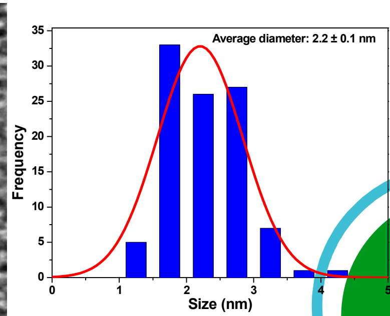
Optimization : precursors, ligands, pH, microwave pulses,…



UV-visible absorption and PL emission spectra of Cu-In-Zn-Se QDs







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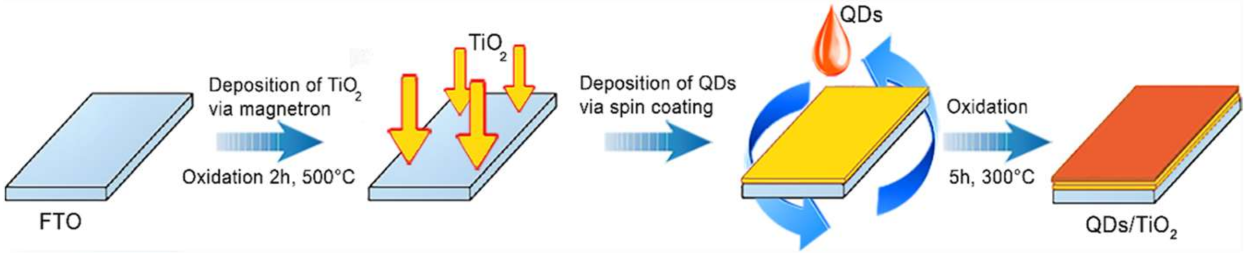
WP1 : Synthesis and optimization of Cu-In-Zn-Se/ZnS QDs –Université de Lorraine & CNRS

Initial screening : Fabrication of QDs/TiO_2/FTO photoelectrode



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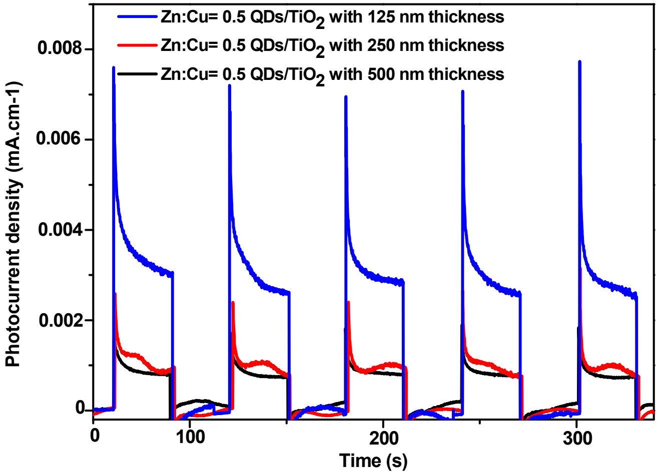

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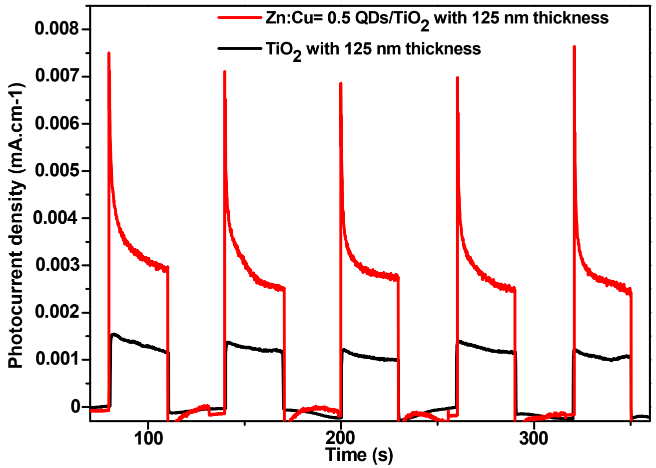

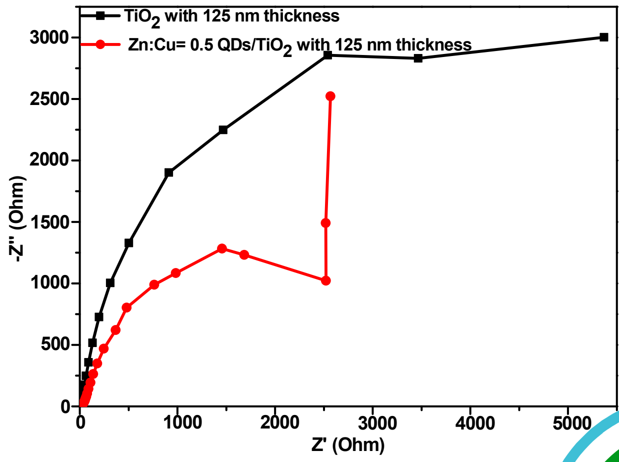

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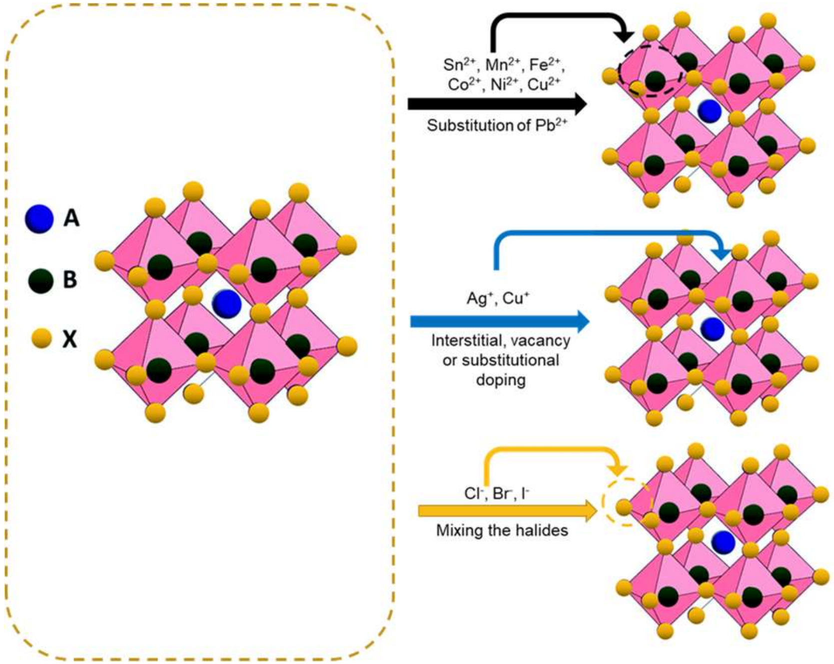
WP1 : Perovskite Nanocrystals - WITS

Objectives

- substitute Pb^{2+} cations with other divalent cations:
  - Sn^{2+} but may be susceptible to oxidation to Sn^{4+}
  - Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}
- Doping of $CsSnX_3$ with Ag^+ and Cu^+ ions.
- Synthesize mixed halides $CsSnX_3$ nanocrystals.
- Use the perovskite nanocrystals as active materials in solar cells.



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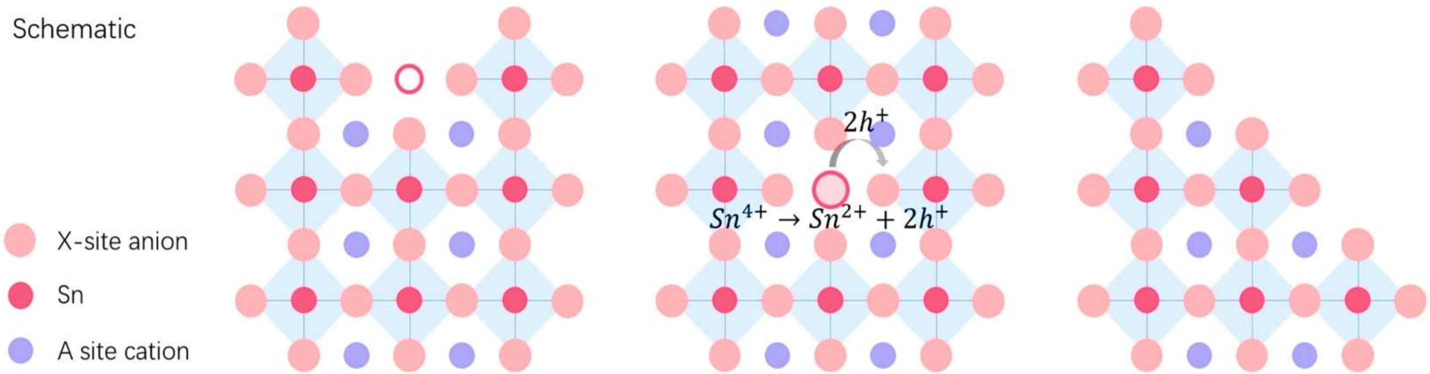
➢ WP1: Perovskite Nanocrystals - WITS

Results

Oxidation of Sn^{2+} to Sn^{4+} in $CsSnX_3$ causes structural instability

Effects of oxidation from Sn^{2+} to Sn^{4+}	Form surface V_{Sn}	Form interior V_{Sn}	Disrupt crystal lattice



Material-level	• Create under-coordinated I ions as non-radiative recombination centers	• Invoke p-type self-doping • Cause high background hole density • Cause high recombination rates	• Degrade perovksite struture
Device-level	• Lower open-circuit voltage	• Lower open-circuit voltage • Lower fill factor	• Impair long-term stability • lead to failure of devices

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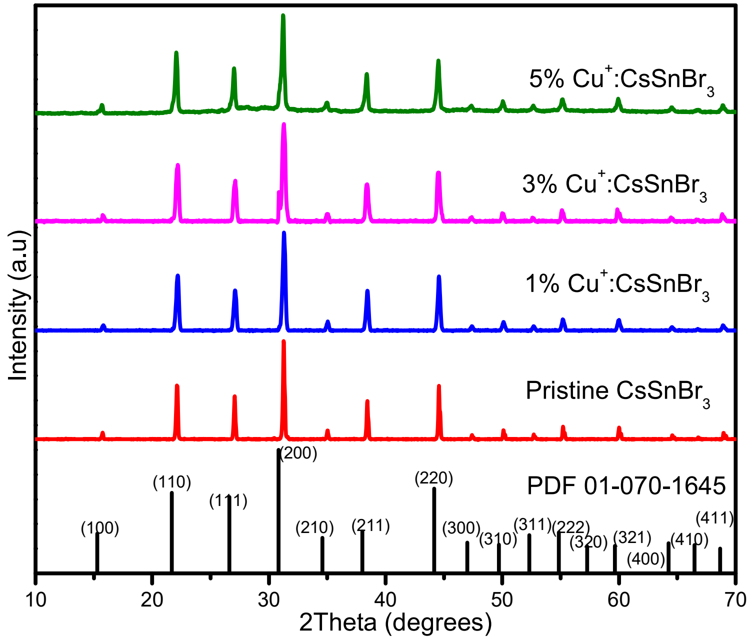
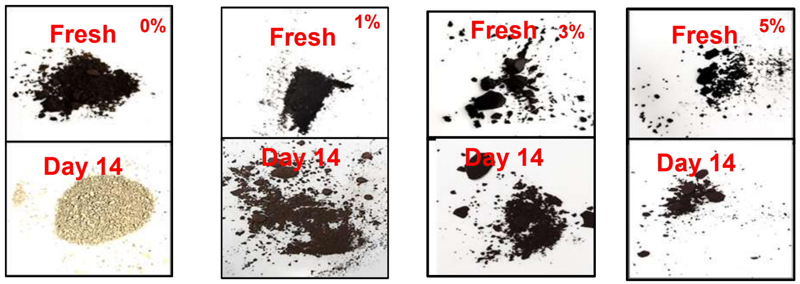
WP1: Perovskite Nanocrystals - WITS

Results : $CsSnX_3$ structural instability can be improved by doping

- XRD patterns of the pristine and Cu^+-doped $CsSnBr_3$, confirming the formation of $CsSnBr_3$.
- A narrowing of the optical band gap as the amount of Cu^+ increased is observed.



- Photographs showing the de-bleaching of the nanomaterials in ambient conditions, the pristine shows instability in Day 14 and the stability improves as the concentration of Cu^+ increases.



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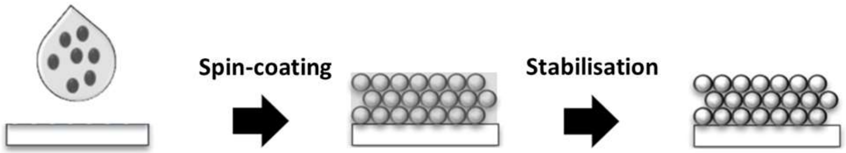
WP2: Development of the TiO_2 photoanode, and optimization of the TiO_2/QDs interface (Liège University)

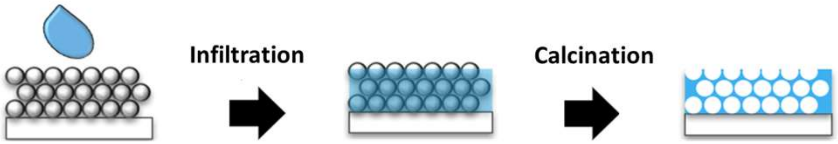
Structuration of the TiO_2 porous layer: Templating strategy

A/ PS beads deposition followed by TiO_2 precursor infiltration
= 2-steps protocol

i) PS beads layer deposition

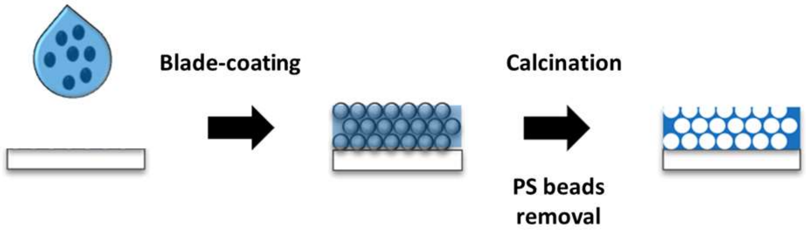


ii) TiO_2 precursor solution infiltration (repeated 4x)

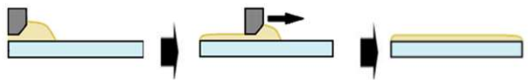


PS beads diameter: *62 nm (=PS62)* **OR** *300 nm (=PS300)*
TiO_2 precursor: *$TiCl_4$ in EtOH*
Deposition technique: *spin-coating*

B/ PS beads in the TiO_2 precursor solution
= 1-step protocol



PS beads diameter: *60nm (=PS60)* **OR** *100nm (=PS100)*
TiO_2 precursor: *18NR-T TiO_2 nanoparticles paste* **OR** *Ti-(iPrO)$_4$ in BuOH (=TTIP)*
Deposition technique: *blade-coating*



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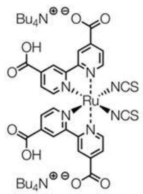
WP2: Development of the TiO_2 photoanode, and optimization of the TiO_2/QDs interface (Liège University)

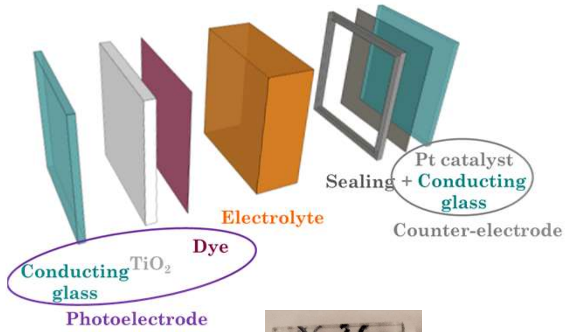
Specific surface determination and first trials in QDSSCs

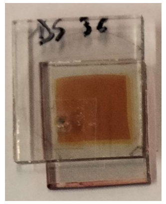
UV-vis colorimetry of N719 desorbed from pre-sensitized TiO_2 porous films by dilute KOH solution

Samples	Thickness (µm)	Specific surface (m^2/cm^3)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PV efficiency (%)	N719 dye loading (mol/mm^3)
18NR-T ref w/o PS beads	1.4	229	0.870	6.5	52	2.8	15.59E-08
18NR-T PS60 1-step	2.2	109	0.711	2.0	70	1.0	7.41E-08
18NR-T PS100 1-step	2.4	168	0.714	6.2	37	1.7	11.43E-08
TTIP PS60 1-step	3.1	61	0.687	1.5	52	0.6	4.13E-08
TTIP PS100 1-step	4.1	45	0.724	2.7	52	1.0	3.05E-08
$TiCl_4$ PS62 2-steps	0.7	124	0.730	1.1	53	0.4	8.42E-08
$TiCl_4$ PS300 2-steps	1	72	0.806	1.2	50	0.5	4.90E-08

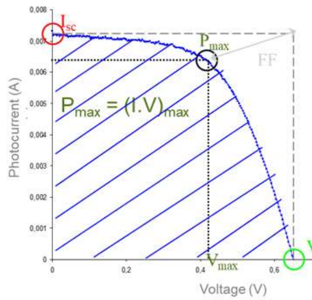
N719 photoactive dye







- Best PV device for 18NR-T w/o PS
- High specific surface with potentially more open porosity vs 18NR-T w/o PS
  ➔ Promising for QDSSCs
- Good efficiency but +2x thicker vs 18NR-T w/o PS
- Very thin layer with time-consuming 2-steps process ➔ Limiting for QDSSCs

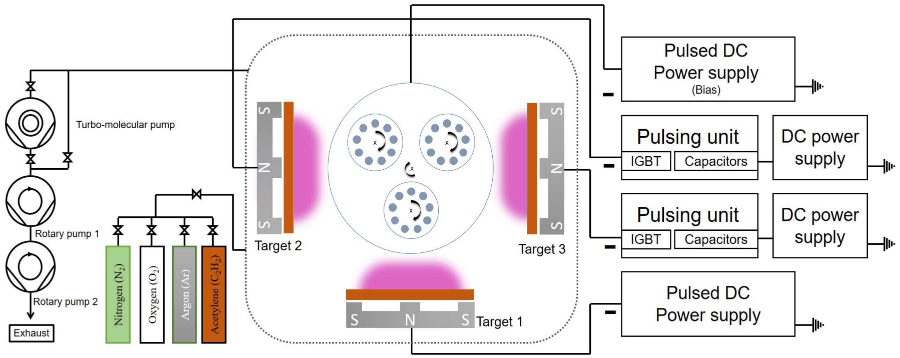


$$FF = \frac{(I.V)_{max}}{I_{sc}V_{oc}}$$

$$\eta = \frac{I_{sc}V_{oc}FF}{P_{incident}}$$

WP2: Synthesis of the dense TiO_2 layer - Mohammed V and Mohamed VI Universities

Industrial-size Cross-Field PVD magnetron sputtering.



Set-up of the vacuum chamber

Process parameters for the DcMS and HiPIMS coatings

Deposition parameters	Constant	
	HiPIMS	DcMS
Duty cycle (%)	5	---
Target dimensions (mm^2)	Ti (568 × 117), 99.99 % pure	
Average power (kW)	3	
Base pressure (mbar)	$\sim 10^{-6}$	
Working pressure (mbar)	10^{-2}	
Distance substrate-target (cm)	6	
Deposition time (min)	45	
Ar flow rate (sccm)	100	
Bias voltage (V)	Floating	
	Variable	
Oxygen flow rate (sccm)	8, 10, 14, 18, 22, 30	

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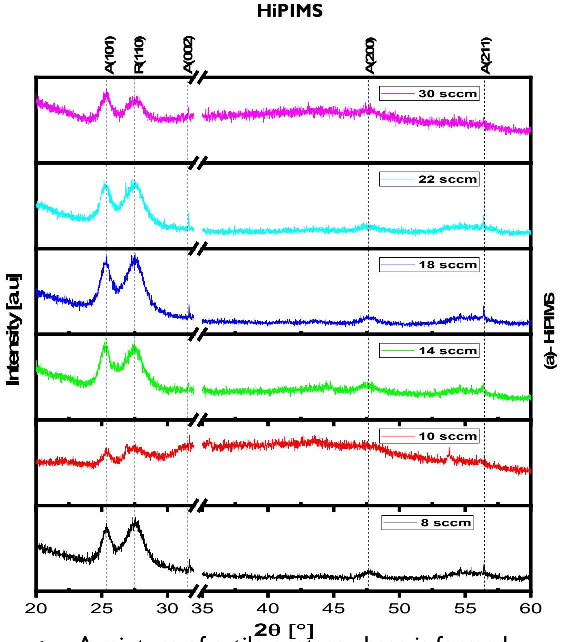
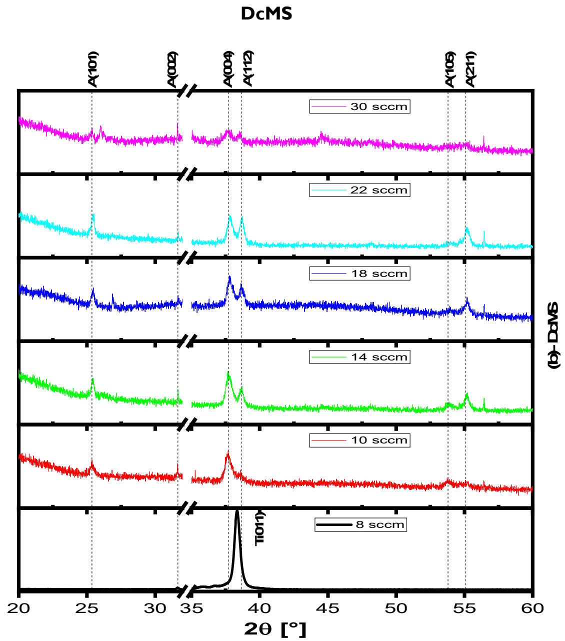
WP2: Synthesis of the dense TiO_2 layer - Mohammed V and Mohamed VI Universities

Morphology & optical properties of TiO_2 films



- A mixture of rutile-anatase phase is formed
- The A(101) and R(110) are prominent

- **High ionization energy associated with HiPIMS results in the ionization of sputtered particles (Ti+ or activated Ti).**
- **Rutile is formed by the reaction of decelerated Ti+ or activated Ti and O2-.**
- **Anatase is produced by the interaction of neutral Ti with neutral O2 and O2- *.**



- Anatase phase is dominant.
- At lower QO2 (8 sccm), the films are still metallic

- **Samples grown using R-HiPIMS present a mixture of anatase and rutile crystalline structures and a pure anatase structure for films deposited using R-DcMS process.**
- **This may be due to ionization fraction of the sputtered species between HiPIMS & DcMS.**

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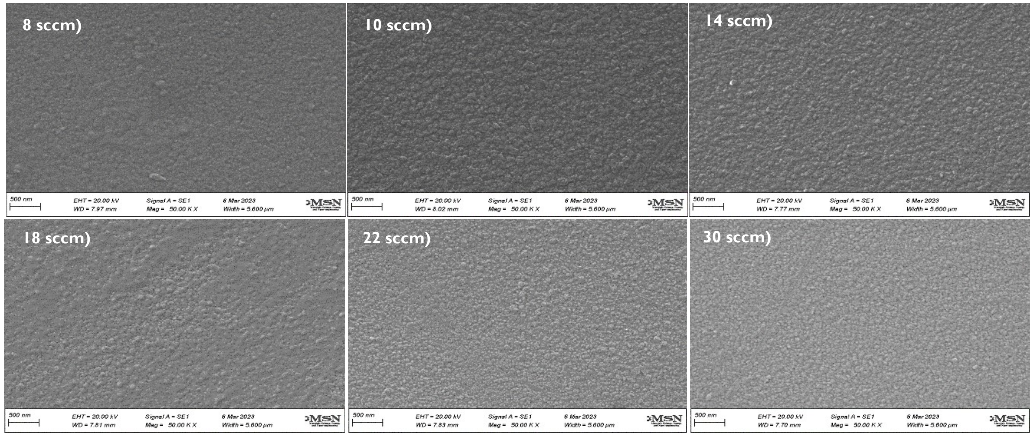
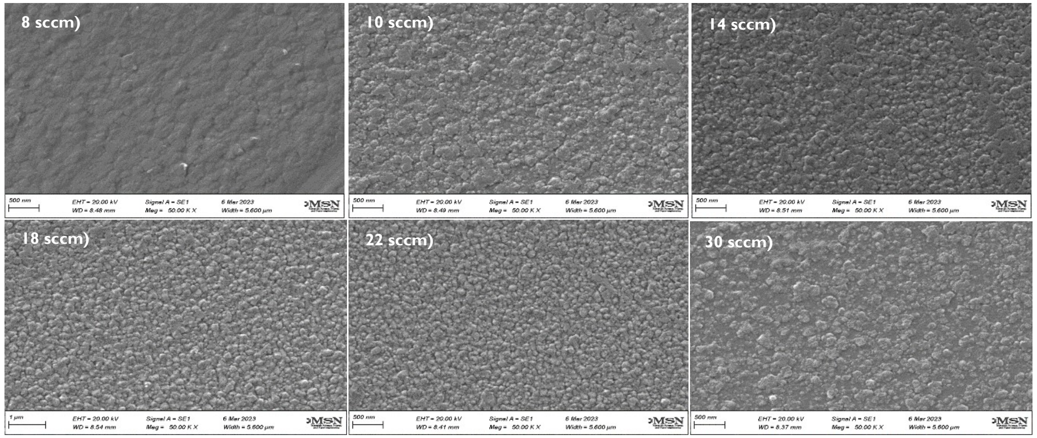
WP2: Synthesis of the dense TiO_2 layer - Mohammed V and Mohamed VI Universities

Morphology



Morphology of TiO_2 deposited by HiPIMS at different O2 flow rates



Morphology of TiO_2 deposited by DcMS at different O2 flow rates

- All films had a dense and crack-free microstructure of spherical-like grains,
- HiPIMS films are denser than the DcMs films due to the increased energy brought on by the incident particles,
- The grain size of the HiPIMS-deposited films is lower than the grain size of the DcMS-deposited films

The **increased ionization rate** provided by **HiPIMS** process causes the ion energy to increase which **enhances the diffusion ability**, increases the nucleation rate, **reduces the grain size**, and increase the grain boundaries*

*Ceram. Int., 2020, doi: 10.1016/j.ceramint.2020.11.175.
*Magnetochemistry, vol. 9, no. 97, 2023.

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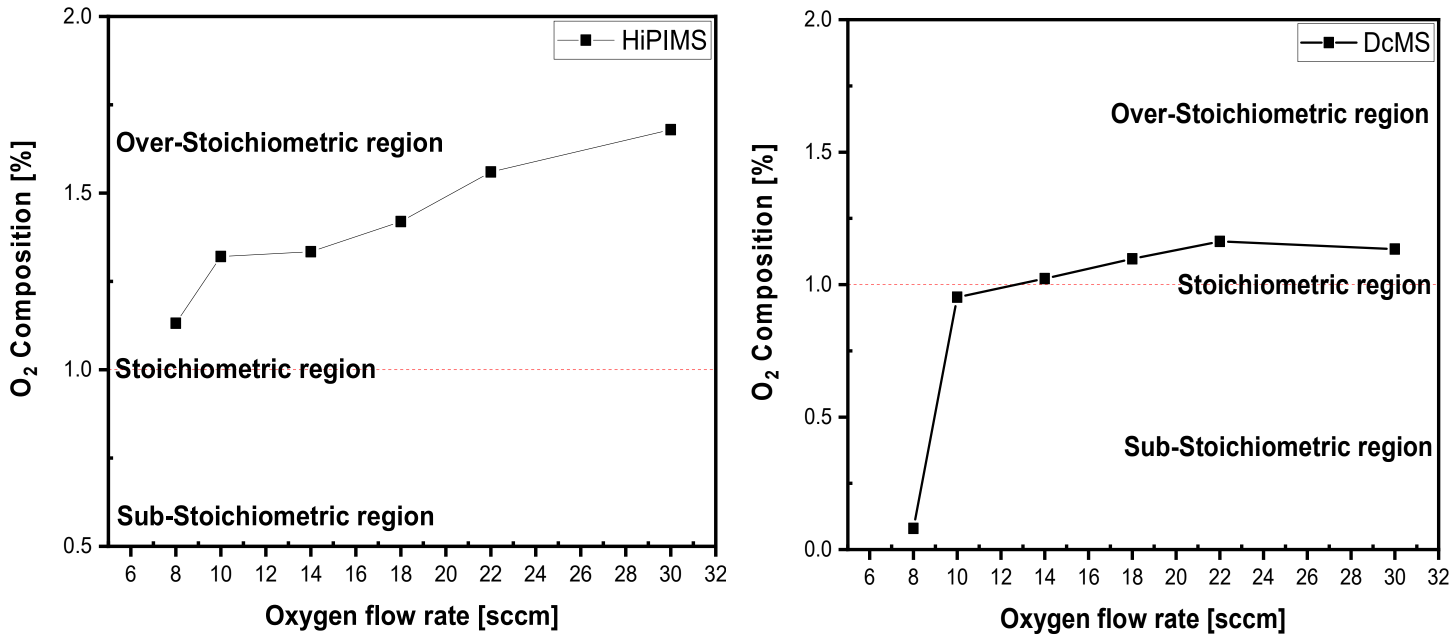
WP2: Synthesis of the dense TiO_2 layer - Mohammed V and Mohamed VI Universities

Elemental Composition



Plot of the fraction composition of Oxygen vs Oxygen flowrate in (right) **HiPIMS** and (left) **DcMS**.

- The oxygen content in all TiOx films is seen to rise as oxygen flow rate rises.
- HiPIMS films are all over-stoichiometric for all oxygen flow rates
- The films deposited above 10 sccm by DcMS showed a change from sub- to over-stoichiometric compositions

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WP3: Solar cell assembly and testing

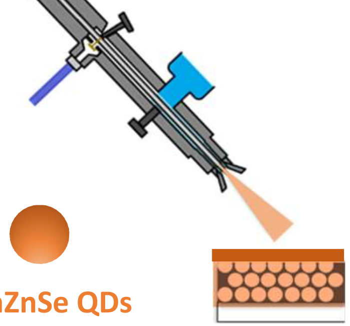
(Liège University)

QDs adsorption trials and first QDSSCs

QDs adsorption protocols (PRs)

PR1
30 min dipping
➔ QDs infiltration inside porous TiO_2

PR2
Air-brush
➔ Dense overlayer of QDs ~ 100 nm thick



CuInZnSe QDs

PR1

PR1+PR2

Calcination 300°C 5h (N_2 atmosphere)

Device assembly

Samples	Thickness (µm)	Specific surface (m²/cm³)	V_{OC} (V)	J_{SC} (mA/cm²)	FF	PV efficiency (%)
18NR-T ref w/o PS beads PR1	1.4	229	0.297	0.2	20	0.01
18NR-T ref w/o PS beads PR1+PR2	1.4	229	0.419	0.6	47	0.1
18NR-T PS100 1-step PR1	2.4	168	0. 181	0.2	24	0.01
18NR-T PS100 1-step PR1+PR2	2.4	168	0.298	0.2	24	0.01

Best PV device with PR1+PR2 and without templating

☹ Low PV parameters for all the devices

➔ hypotheses:

i) Reduced charge transfer between TiO_2/QDs or QDs/QDs

ii) Issue in counter electrode preparation (lack of uniformity of the catalyst on the TCO glass)

➔ perspectives:

i) Charge transfer improvement through a thin ZnS overlayer deposition

ii) Improvement of the counter-electrode uniformity

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- *End of project expected results (2025)*

  - ***Planned follow-up work, new pathway to explore…***
  - **Depending on the results obtained after integration of QDs in QDSSCs, new nanocrystals may be explored (variation of composition, shell, surface ligand,…)**
  - **Modification of the QDSSC configuration (counter electrode,…)**
  - **Development of a QDSSC prototype to validate the concept of this project**

  - ***Become of the consortium set up on this project***
  - **We hope that the results of this project will allow us to continue the collaboration**

  - ***New collaborations initiated thanks to the results of the project (following publications, conference presentations, etc.)***
  - **Nothing programmed to date**

  - ***New collaborations planned for the future (to answer what problem? Industrial or other perspectives?…)***
  - **Nothing programmed to date. Possible evolution according to our results in 2024**

  - ***New funded projects and/or funding applications (what type(s) of funding?)***
  - **Nothing programmed to date**

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Expected outcomes in case of success of the project (2030)

What could be the impact of the project at 2030 on the economy and/or society in case of scaling up the results of the project ?

Social benefits:

(1) Develop reliable stand-alone system architecture that can be easily and widely deployed in off-grid African rural and remote areas, thus giving access to affordable energies to the largest number of beneficiaries.

(2) Integrate renewable energies into the global energy mix through versatile, stand-alone systems and to help to address the energy needs of off-grid areas in Africa.

Economic benefits:

(1) faster, less costly approach to discover and assess new materials for PV devices,

(2) better design photovoltaic cells to make more efficient solar panels and lower the cost of generating clean and renewable electricity,

(3) reduction of the disposal and recycling related-cost of the PV cells by a backward integration of the environmental regulation standards during the manufacturing stage.

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Contribution of the project to AU – EU R&D partnership

In term of reinforcement of scientific or innovation cooperation, capacity building…

- QDSOC will contribute to strengthen African and European competitiveness in the materials science and engineering sector, allowing for a rapid translation of results from laboratory and pilot test plants to the market and thus impacting different areas such as environmental, economic, social and scientific communities.

Interest of Consortium members in participating in LEAP-RE clustering activities

Which thematic (MARs technologies…) or methodology (modelling, on site experimentation…) members would be interested to share with other LEAP-RE projects ?

THANK YOU

CONTACT US FOR MORE INFORMATION

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