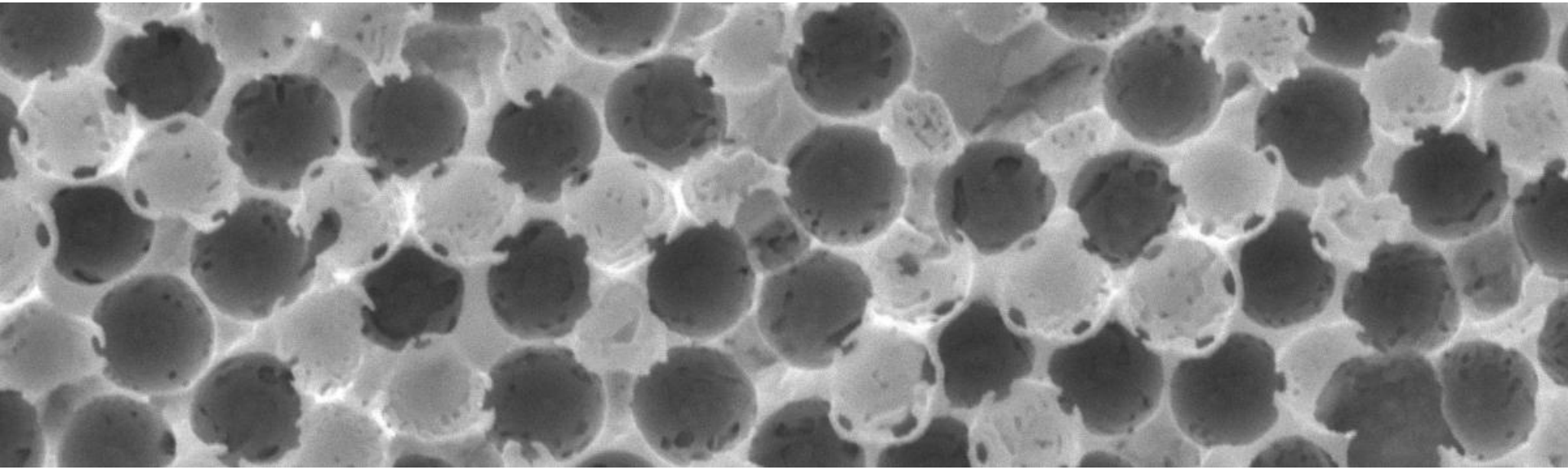
Influence of the microstructure and doping of $CH_3NH_3PbI_3$ and $CH_3NH_3PbI_{3-x}Cl_x$ films as photoelectrodes in perovskite-based photovoltaic cells



Promoter : Jennifer DEWALQUE

Co-promoter : Catherine HENRIST

Dissertation submitted by **Nathan Daem**

To obtain the grade of

Master in Chemical Sciences

Academic Year 2017-2018

I. Introduction

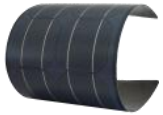
Photovoltaic technologies

1st generation

- Mono or polycristalline Silicon

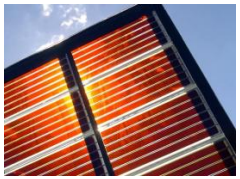
2nd generation

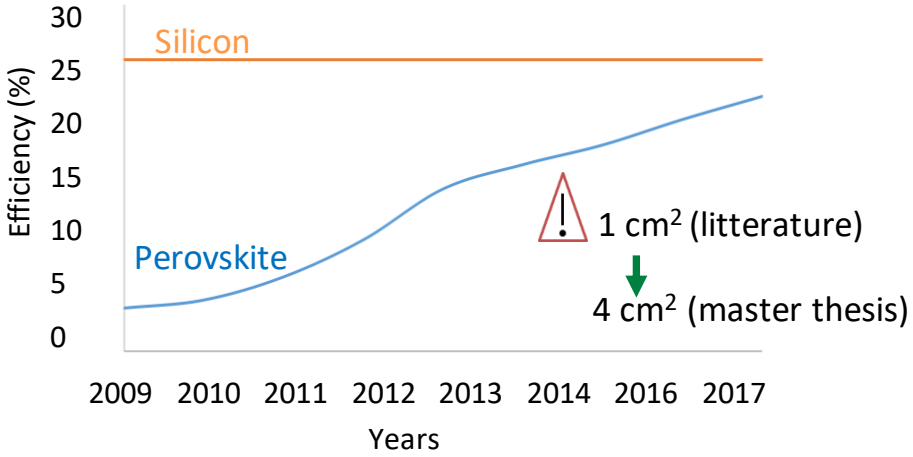
- Thin films : CIGS, CdTe, a-Si



3rd generation

- Organic solar cells
- Dye-sensitized solar cells
- Perovskite solar cells





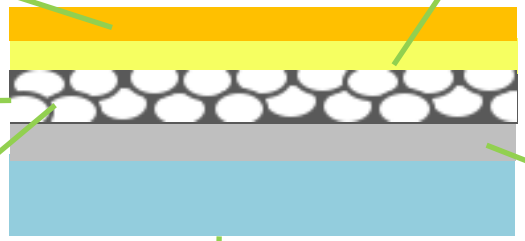
http://www.nrel.gov/pv/

- ✓ High absorption coefficient over the visible solar spectrum
- ✓ Low cost manufacturing process and raw materials
- ✘ UV and moisture sensitive
- ✘ Contains lead ($CH_3NH_3PbI_3$)

Perovskite-based PV cell consitutants

Counter-electrode
→ Gold

Hole transporting material
→ Spiro-MeOTAD

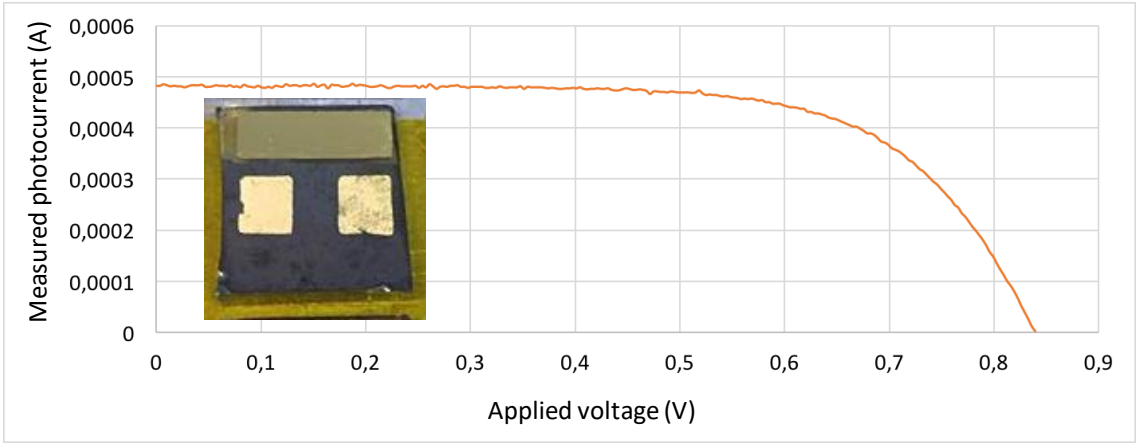


Perovskite
→ $CH_3NH_3PbI_3$, $CH_3NH_3PbI_{3-x}Cl_x$
→ Absorbs light, creates electron-hole pairs

Dense TiO_2
→ Avoids short-cuts

Substrate
→ FTO conducting glass

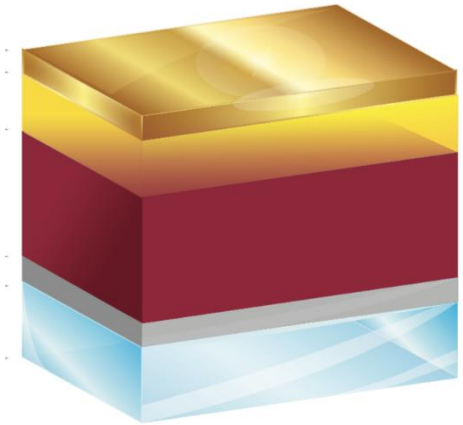
Mesoporous TiO_2
→ Filled by the perovskite
→ Collects the electrons



II. Objectives

Part A:

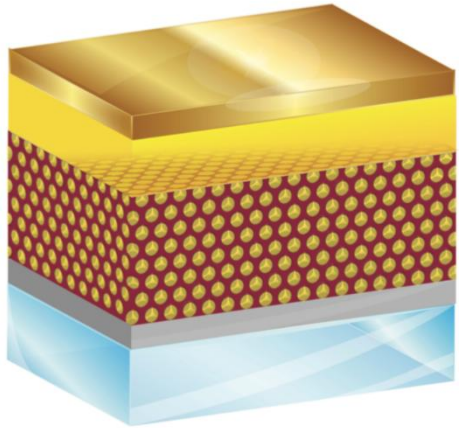
Dense perovskite



Objective: $\eta > 10\ \%$

Part B:

Porous perovskite

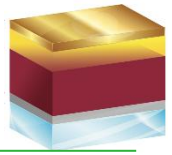


Objectives:

- Coloration
- Effect of 3D structuration on η

III. Strategy

Part A – Dense –1 step/2 steps deposition process



CH_3NH_3I (MAI) + PbI_2 → $CH_3NH_3PbI_3$

1 STEP :

Pb + MAI precursors

Spin coating

Stabilization

2 STEPS :

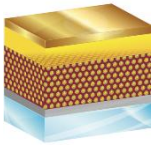
Pb precursor

Spin coating

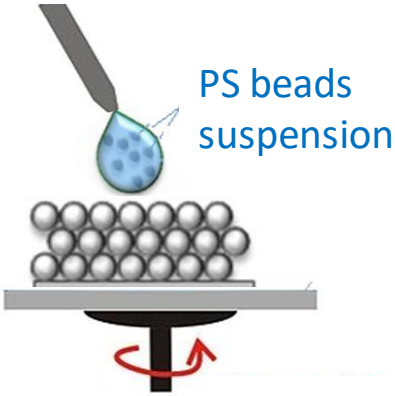
Immersion MAI solution

Stabilization

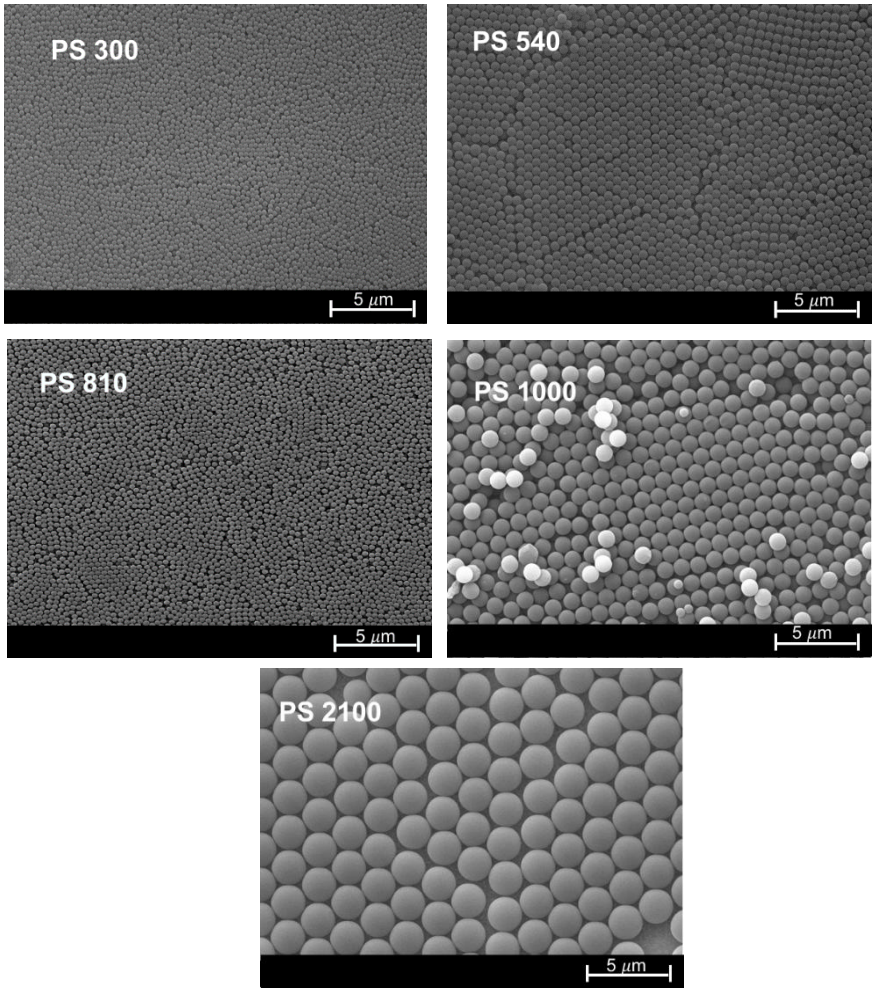
Part B – Porous – Templating method



1st step : PS beads layer deposition

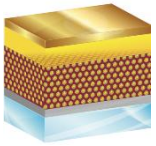


Stabilization

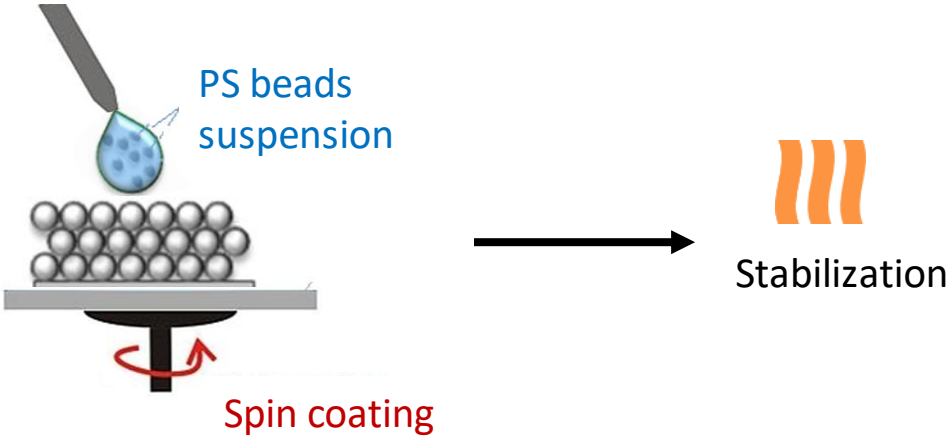


→ Well organized and high coverage PS beads layers

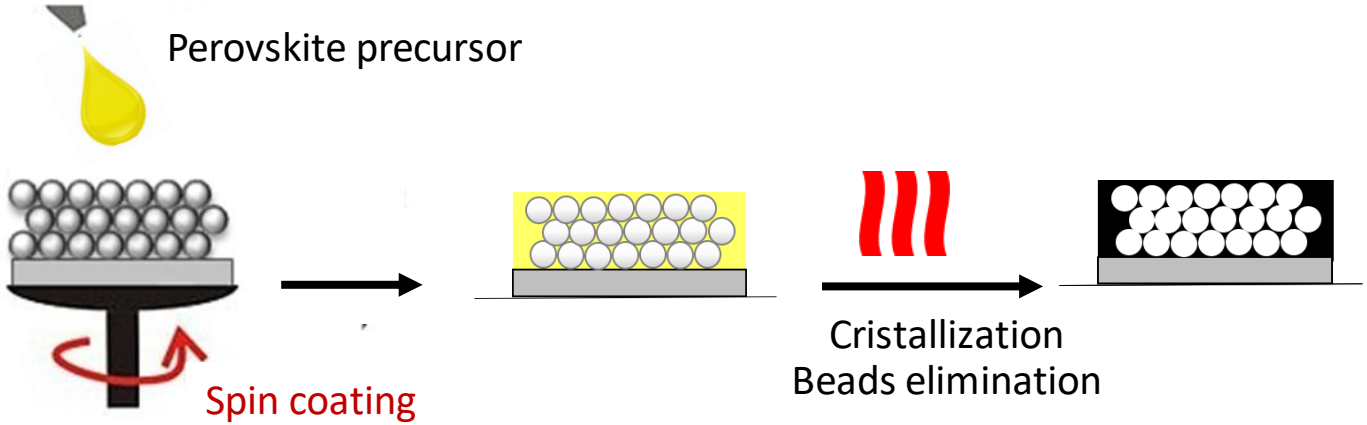
Part B – Porous – Templating method

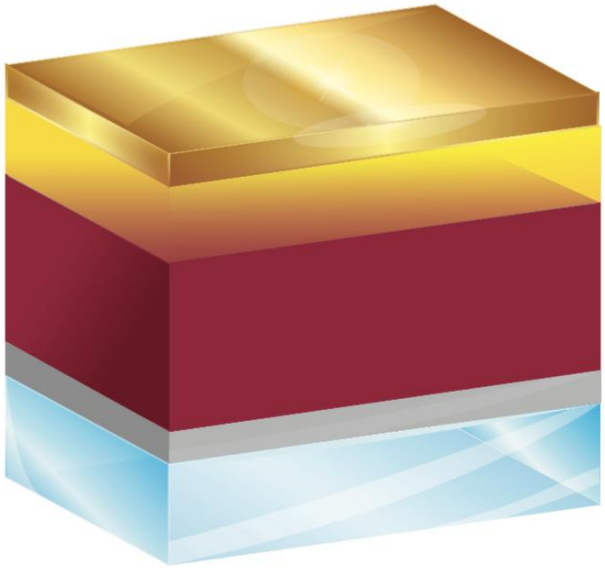


1st step : PS beads layer deposition



2nd step : perovskite infiltration (1-step process)



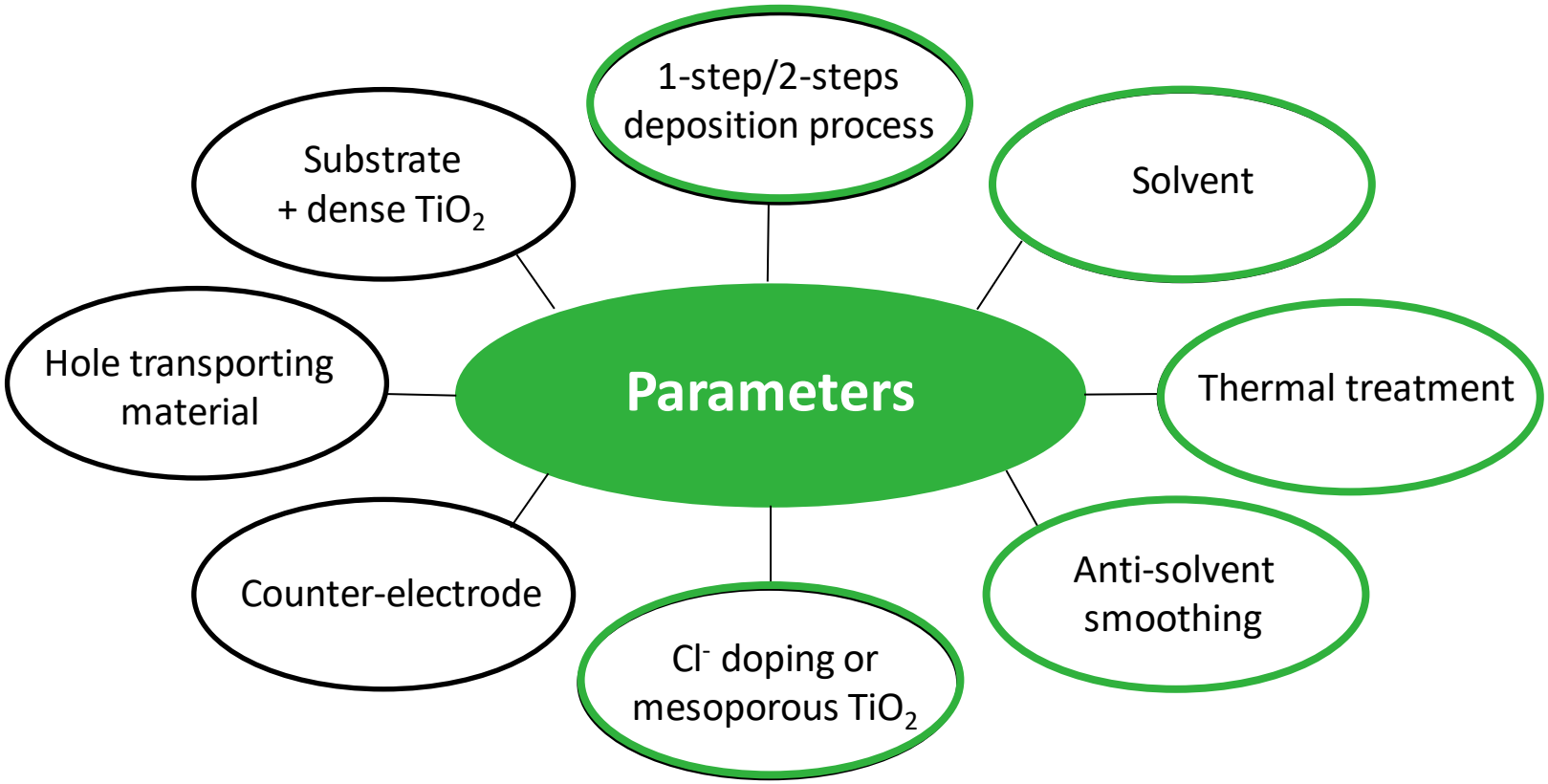


IV. Results

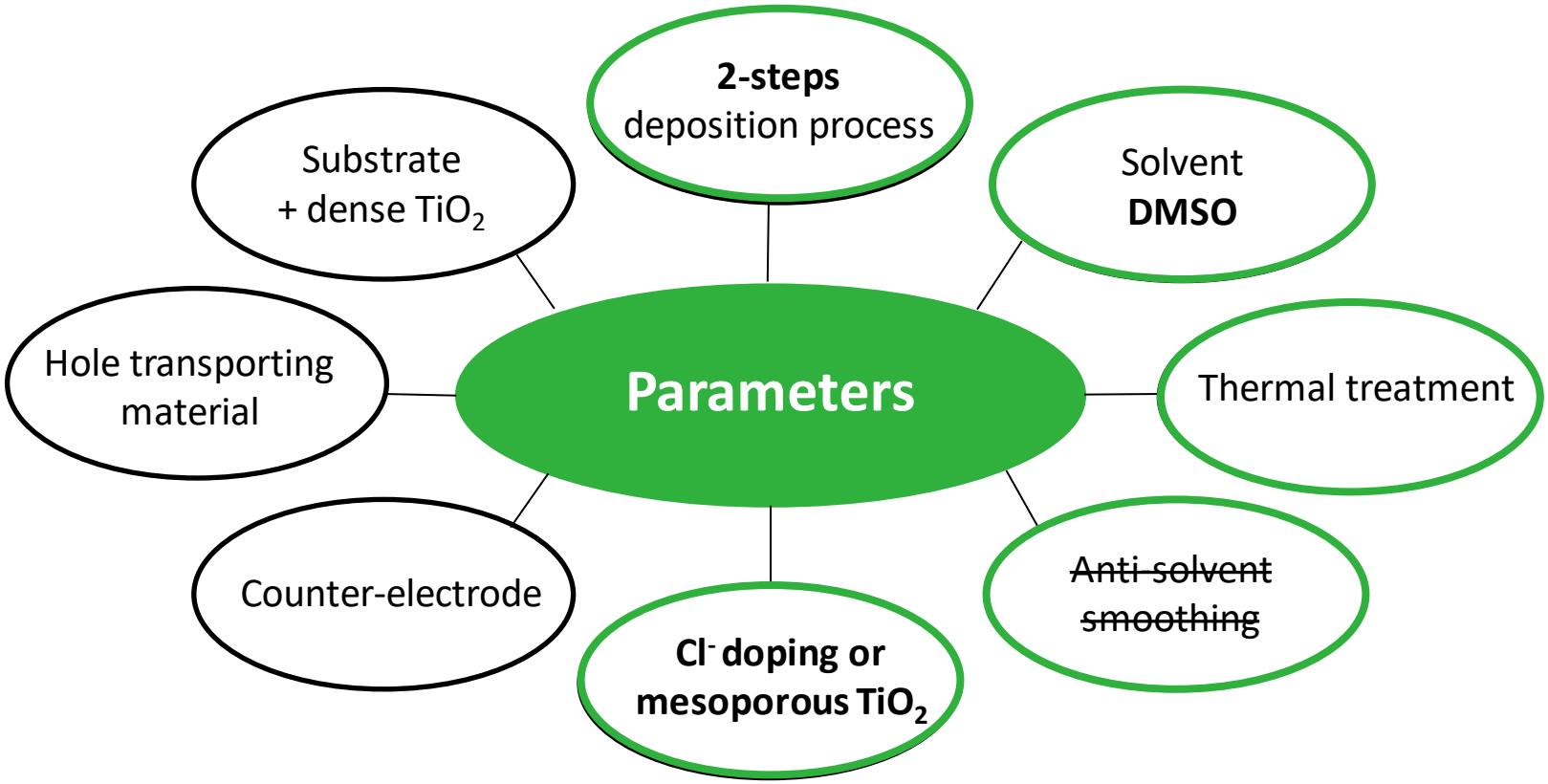
A. Dense perovskite

B. Porous perovskite

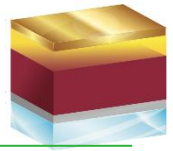
Experimental parameters



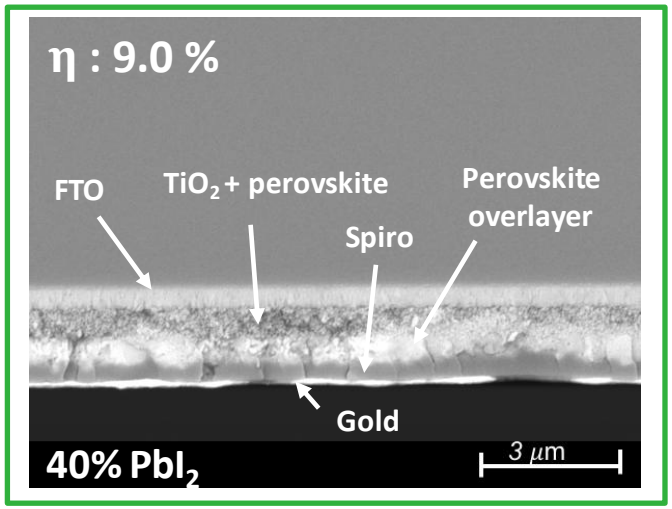
Best parameters



Mesoporous TiO_2 (WITHOUT doping) – electron collector



Experimental parameters	
Deposition process	2 steps
Solvent	DMSO
PbI_2 Film	40 wt%
Conversion	Immersion in a MAI solution
Thermal treatment	15 min 75°C



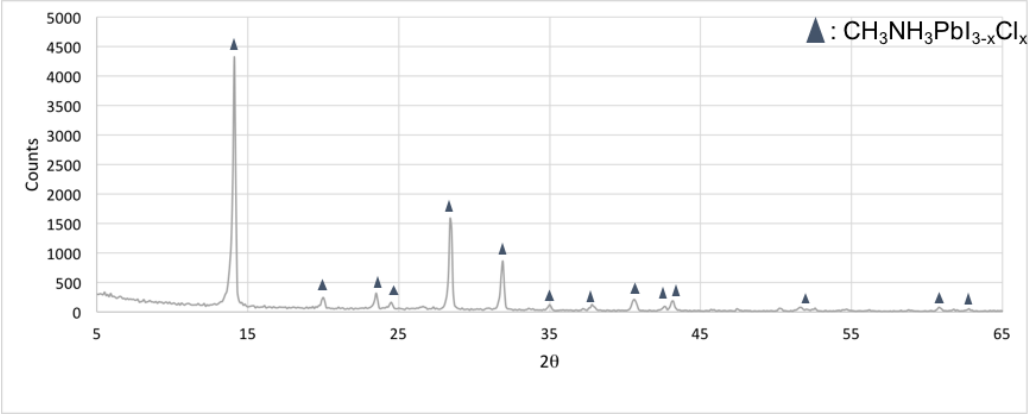
Without mesoporous TiO_2 : η: 0.1 %

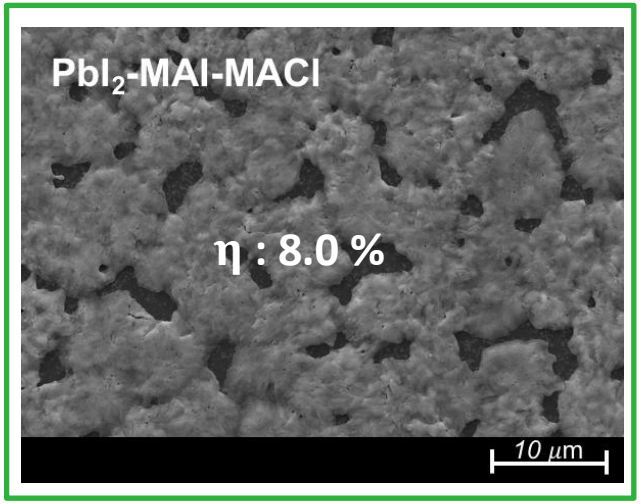
Efficiency improvement :
→ Electron transfer within mesoporous TiO_2

✓ Champion cell : **η : 11.0 %**

Cl^- doping

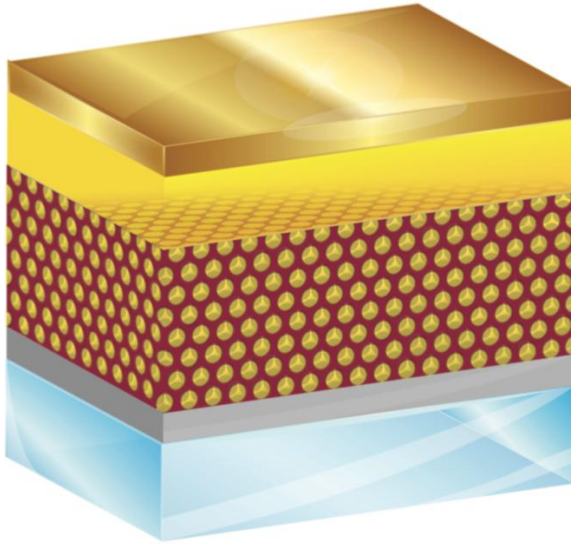
Experimental parameters	
Deposition process	2 steps
Solvent	DMSO
Solution	PbI_2 + MAI:MACl
Thermal treatment	15 min 135°C





No thickness limitation related to charge diffusion length

✓ Champion cell : **η : 12.1 %**

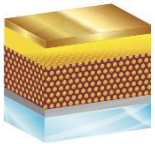


IV. Results

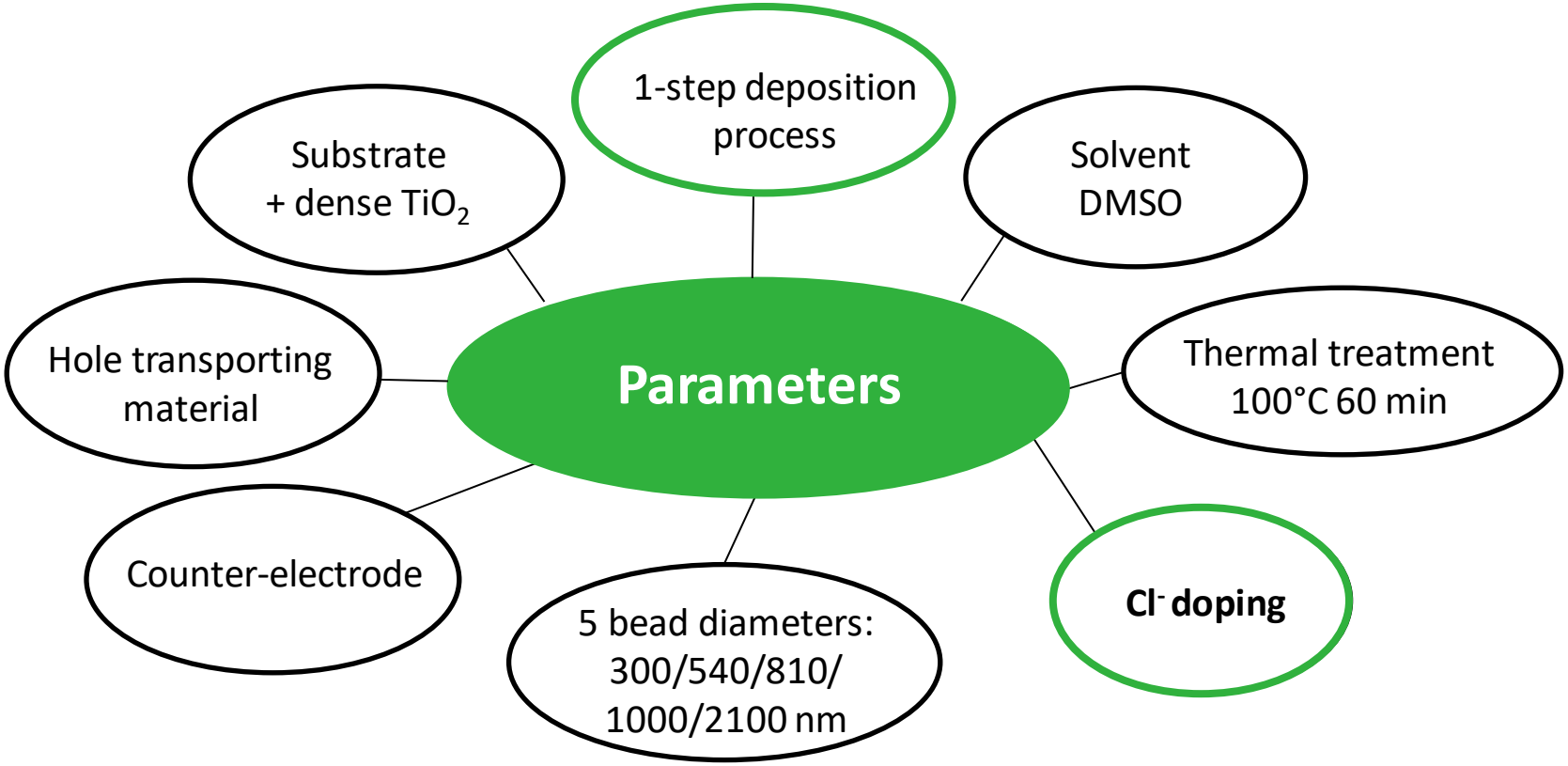
A. Dense perovskite

B. Porous perovskite

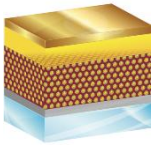
Experimental parameters



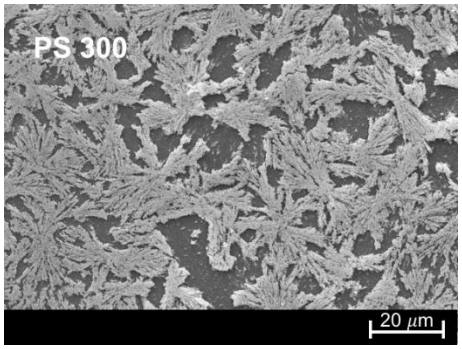
Studied parameter : precursor solution concentration and doping

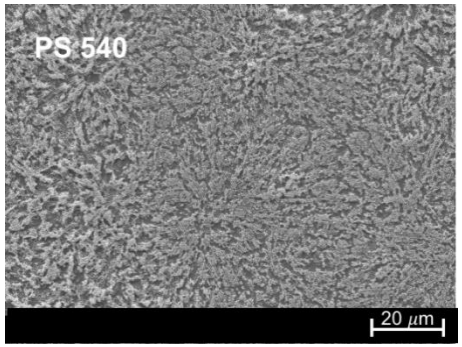


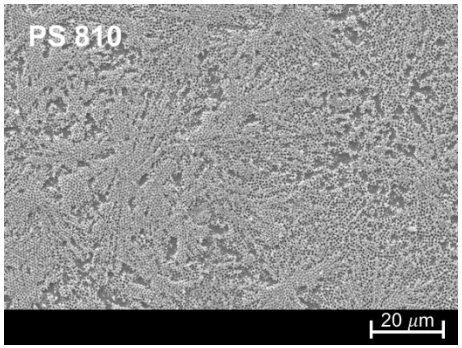
Concentration

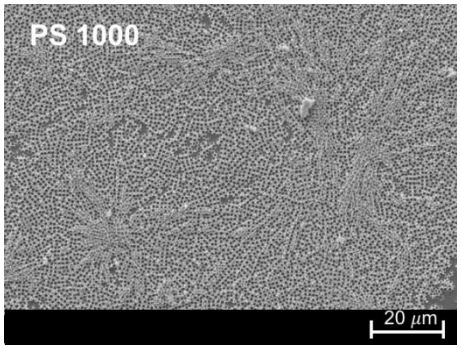


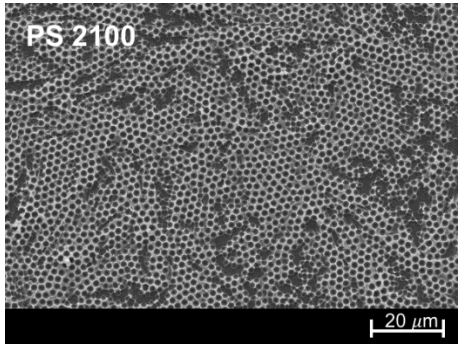
Optimal concentration PbI_2/ MAI: **0.7 M**



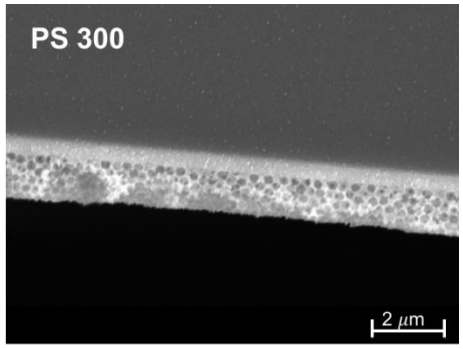


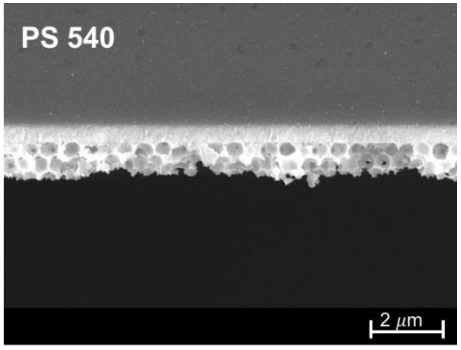


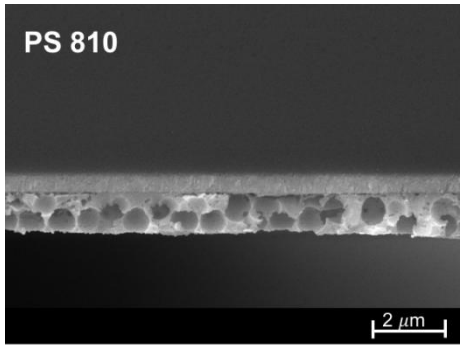


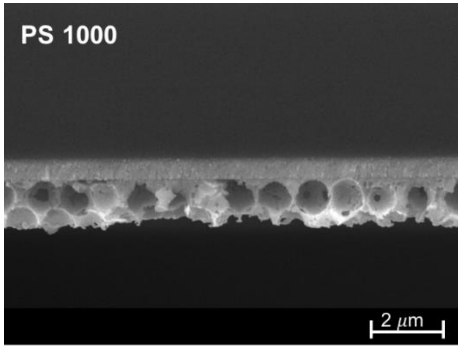


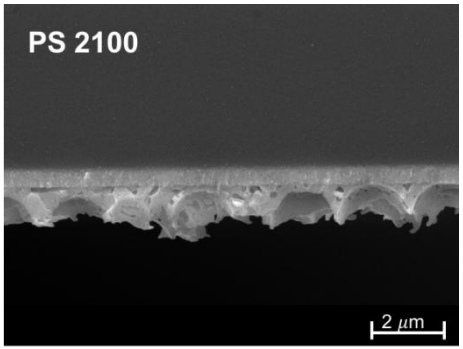
Thickness : 1.0 -1.2 µm



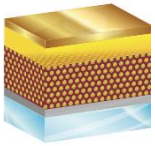




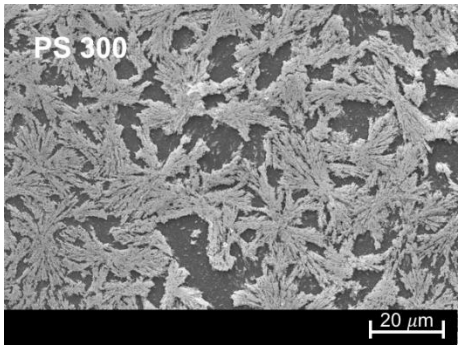


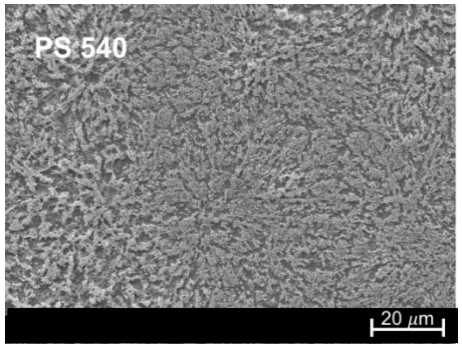


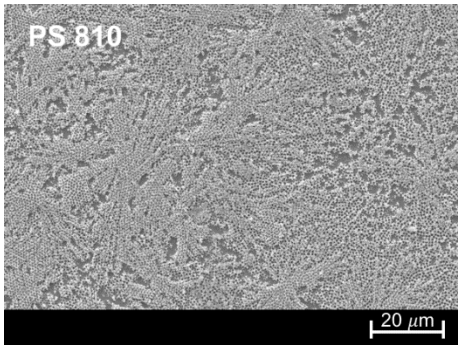
Concentration

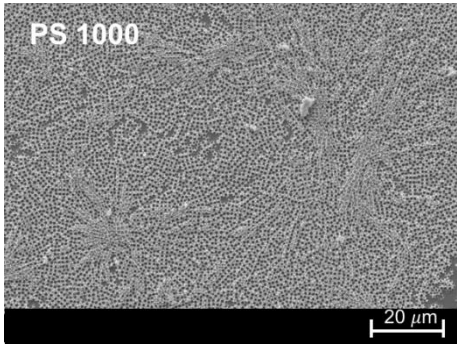


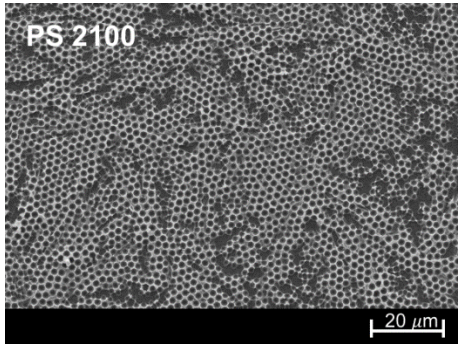
Optimal concentration PbI_2/ MAI: **0.7 M**





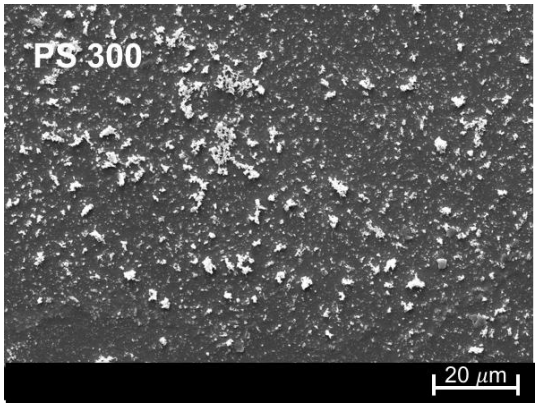






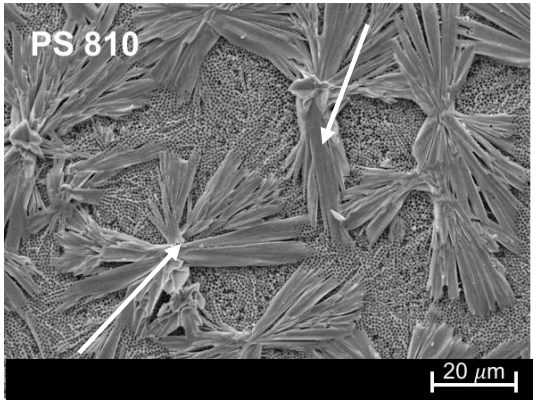
If concentration < **0.7 M**

→ Not uniform and poor coverage films



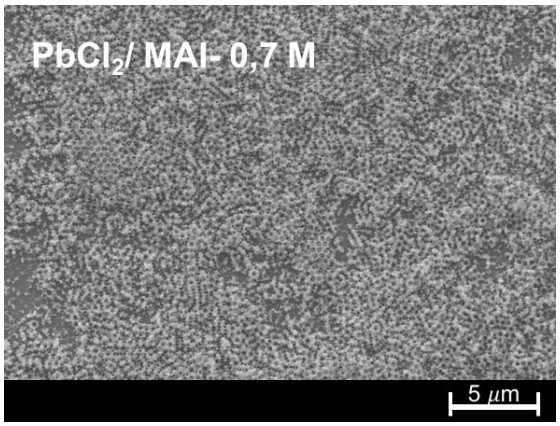
If concentration > **0.7 M**

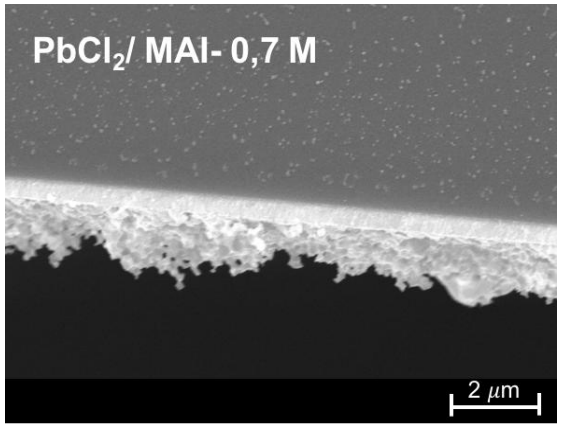
→ Dense perovskite overlayer

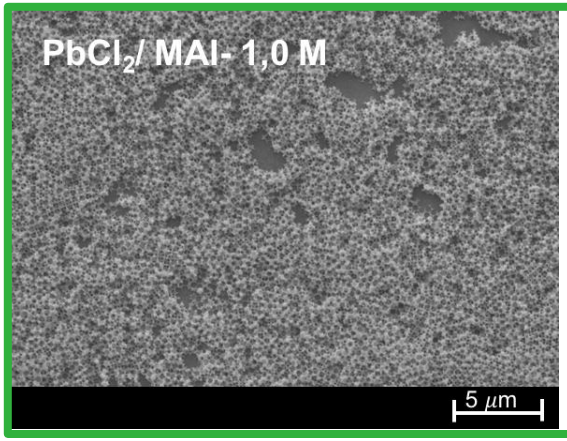


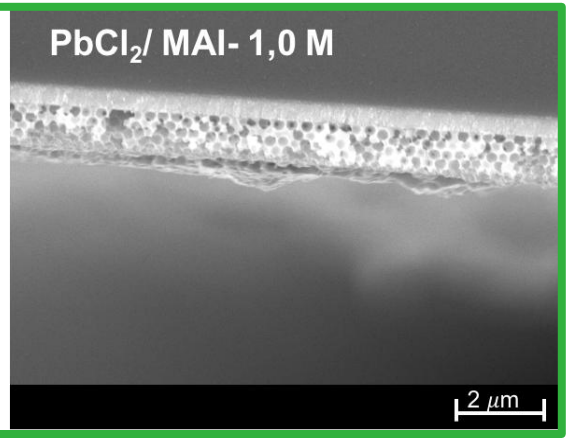
Doping + concentration

Use of $PbCl_2$ as chlorine source :





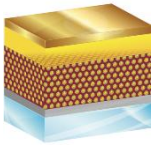




Thickness : 1.0-1.3 µm

NO perovskite overlayer and more uniform films with $PbCl_2$/MAI 1.0 M ➔ Cells assembly

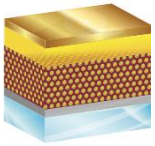
PV efficiencies



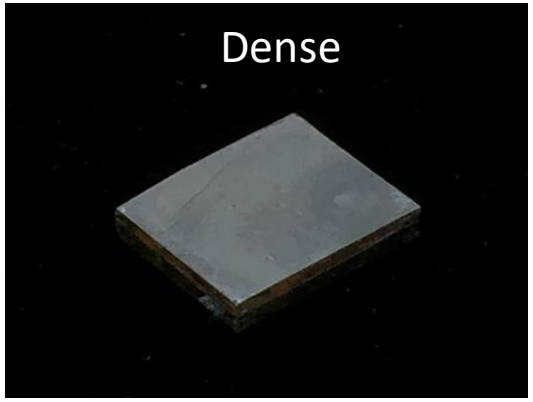
	DENSE	PS 300	PS 540	PS 810	PS 1000	PS 2100	∅ PS beads
WITHOUT doping	0.1 %	1.0 %	1.1 %	1.9 %	0.8 %	2.3 %	η (%)
WITH doping	8.0 %	1.1 %	1.6 %	2.2 %	3.0 %	2.5 %	η (%)

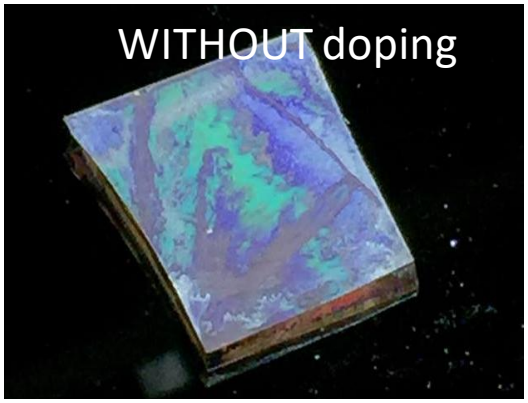
- Efficiency improvement with PS bead diameters
- Doping effect not obvious (>< Dense)
- Efficiency improvement due to 3D structuration (>< Dense WITHOUT doping)

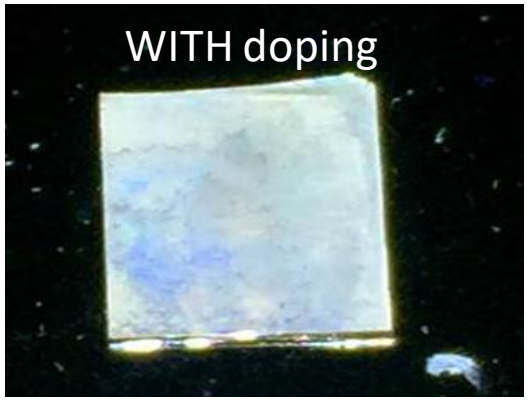
PV efficiencies



	DENSE	PS 300	PS 540	PS 810	PS 1000	PS 2100	∅ PS beads
WITHOUT doping	0.1 %	1.0 %	1.1 %	1.9 %	0.8 %	2.3 %	η (%)
WITH doping	8.0 %	1.1 %	1.6 %	2.2 %	3.0 %	2.5 %	η (%)





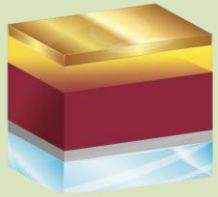


Coloration of illuminated films on silicon substrates

✓ Building integration

V. Conclusions

Dense perovskite

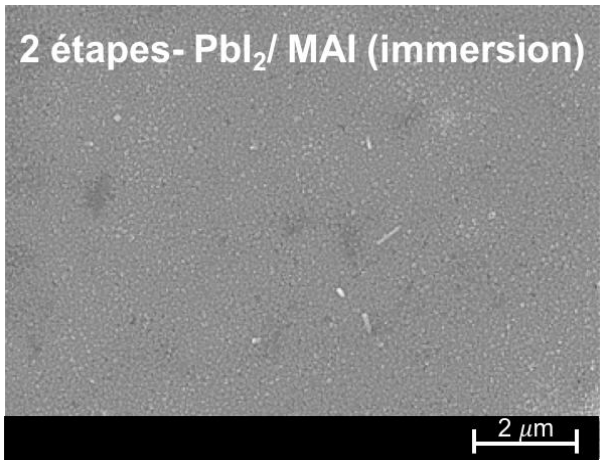


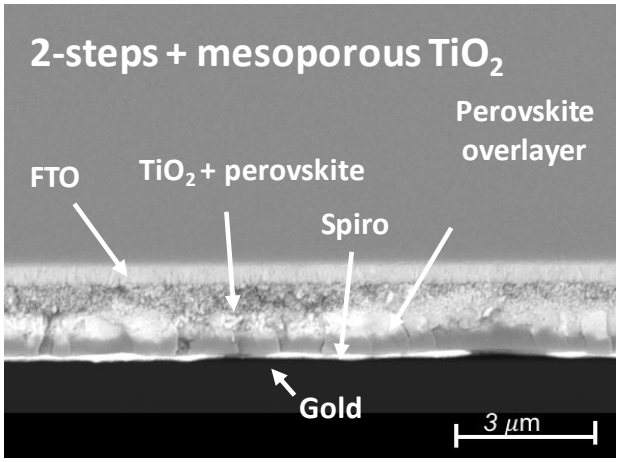
✓ **Goal :** η > 10 %

BUT mesoporous TiO_2 /doping required

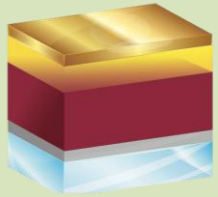
Champion cell : **η : 11.0 %**

Champion cell: **η : 12.1 %**



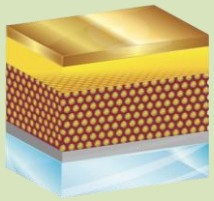


Dense perovskite

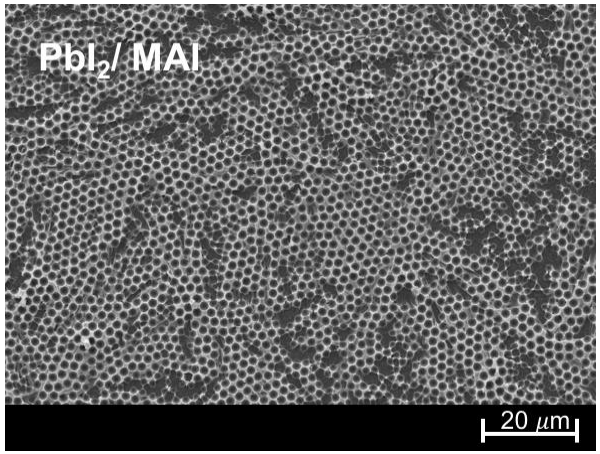


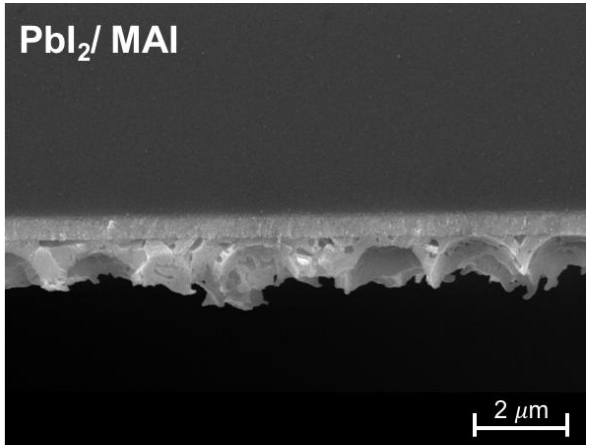
✓ **Goal :** $\eta > 10\ \%$
BUT doping /mesoporous TiO_2 required

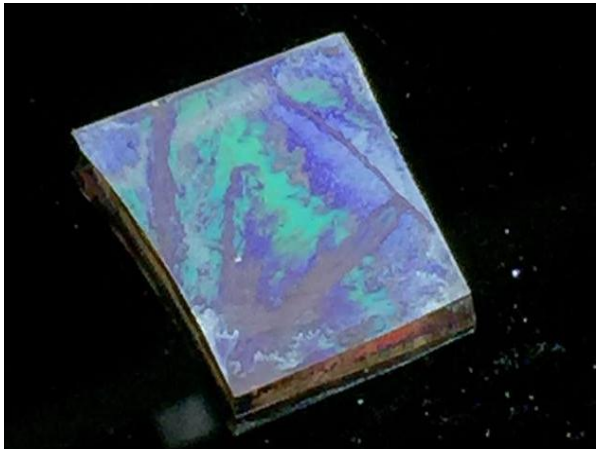
Porous perovskite



✓ **Goal :** coloration and ↗ η with 3D structuration
(>< Dense WITHOUT doping)







Thank you for your attention

Thank to everyone who has contributed directly or indirectly to this master thesis