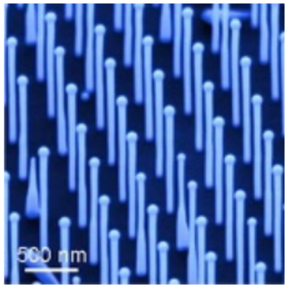

ELaboration of NANOmaterials for the recovery, conversion, transport and storage of energy

11-16 Jun 2023 Aussois (73500) (France)

Chemical Solution Deposition Processes: A Short Overview

Fabien Grasset

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13th June 2023, El NANO

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Curriculum Vitae

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DUPONT

07-08/1998
Invited researcher

01-03/2007
Invited researcher

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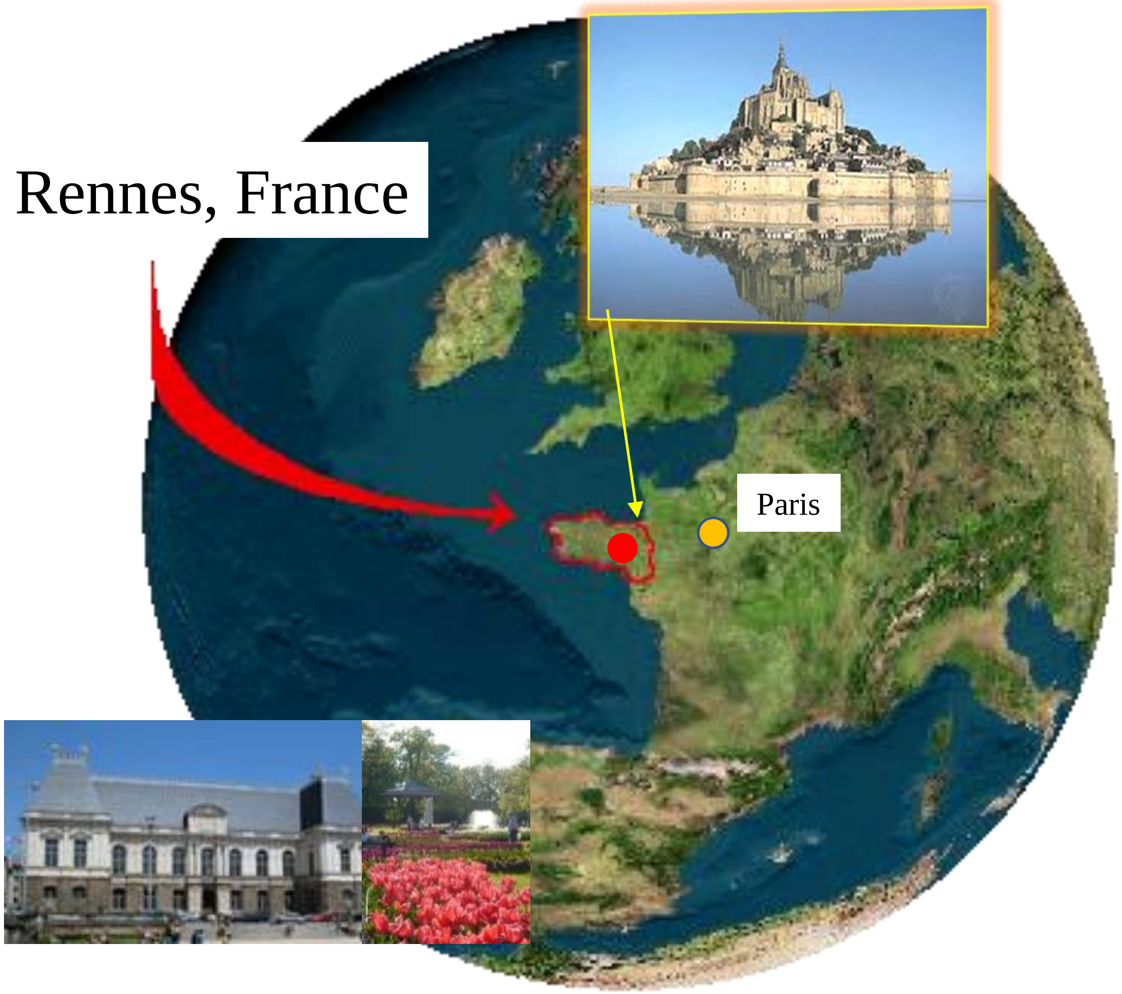
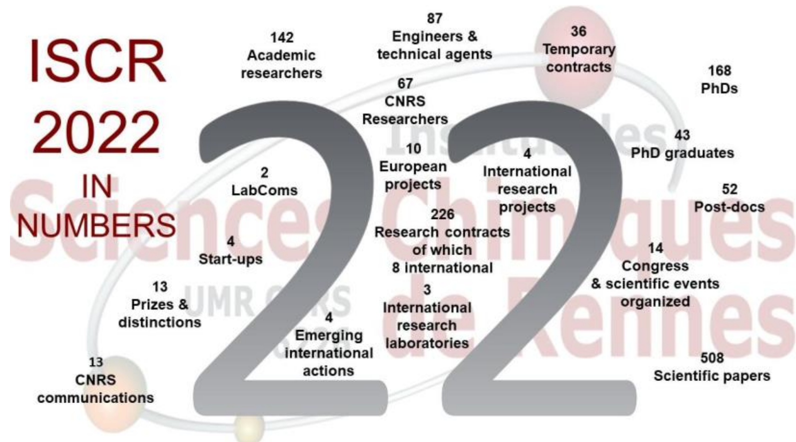
13th June 2023, EI NANO

Université de Rennes





~290 permanent staffs

~300 non-permanent staffs

NIMS SAINT-GOBAIN cnrs

Link IRL 3629

Laboratory for Innovative Key Materials & Structures, LINK, St Gobain K.K. and NIMS, ***Partnership with industry, 2014***

cnrs

Fabien Grasset

13th June 2023, EI NANO

Outline

1) Introduction

2) Spin-Coating

3) Dip-Coating

4) Mayer bare coating

5) Spray-Coating

6) EPD

7) Conclusion

Outline

1) Introduction

2) Spin-Coating

3) Dip-Coating

4) Mayer bare coating

5) Spray-Coating

6) EPD

7) Conclusion

1) Introduction

Objectives:

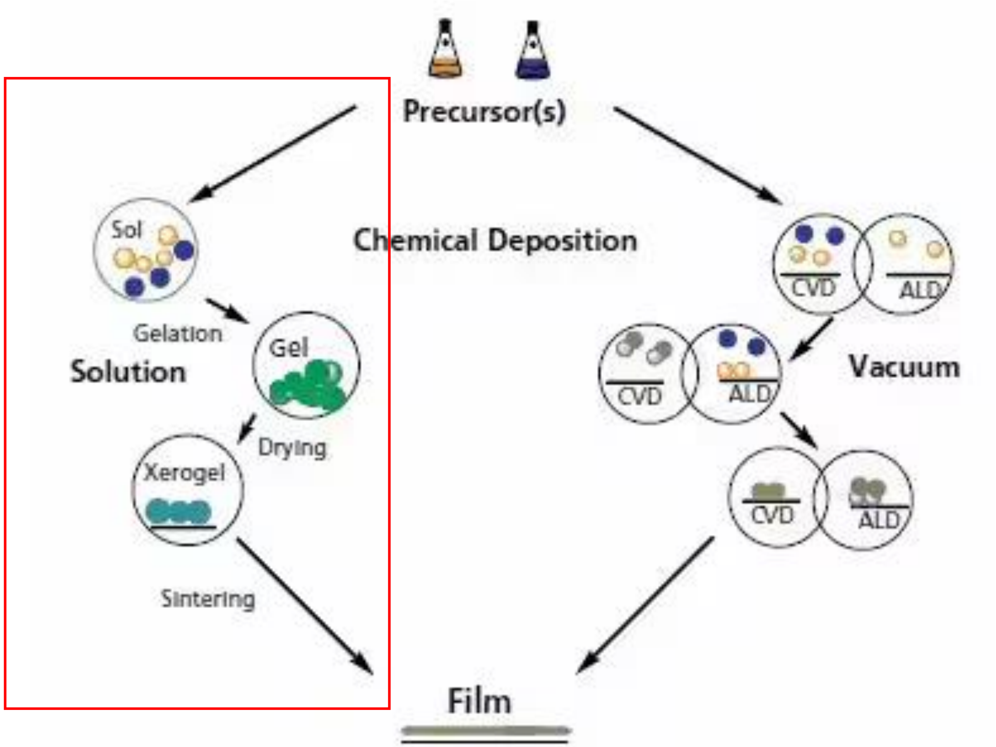
-To introduce some basic concepts of synthetic chemical solution deposition (CSD) techniques and processing with high potential for deposition of advanced material thin films.

-To show that the preparation of innovative materials using CSD routes is a growing technological area.

1) Introduction

Definition:

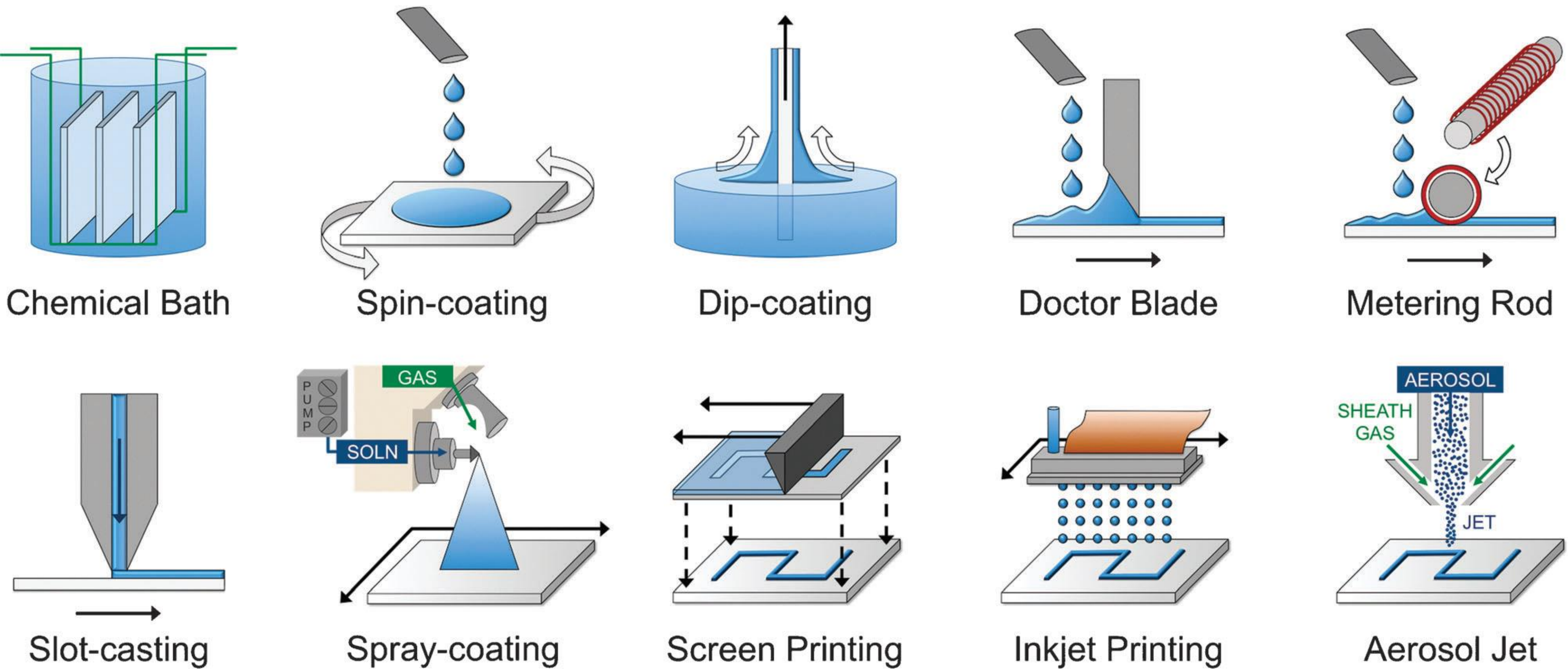
-Chemical solution deposition (CSD) processes: CSD is a general term used to describe any technique whereby a chemical precursor solution is used to create a film.



Schematic illustrating chemical deposition of ceramic films.
(from https://www.sigmaaldrich.com/FR/en/technical-documents/technical-article/materials-science-and-engineering/photovoltaics-and-solar-cells/chemical-deposition)

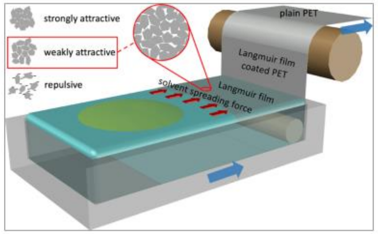
1) Introduction

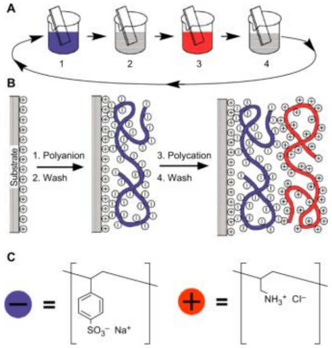
Depiction of various CSD deposition methods (there are more…)



From Chem. Soc. Rev., 2011, **40**, 5406–5441

Langmuir-Blodgett, Layer-by-Layer

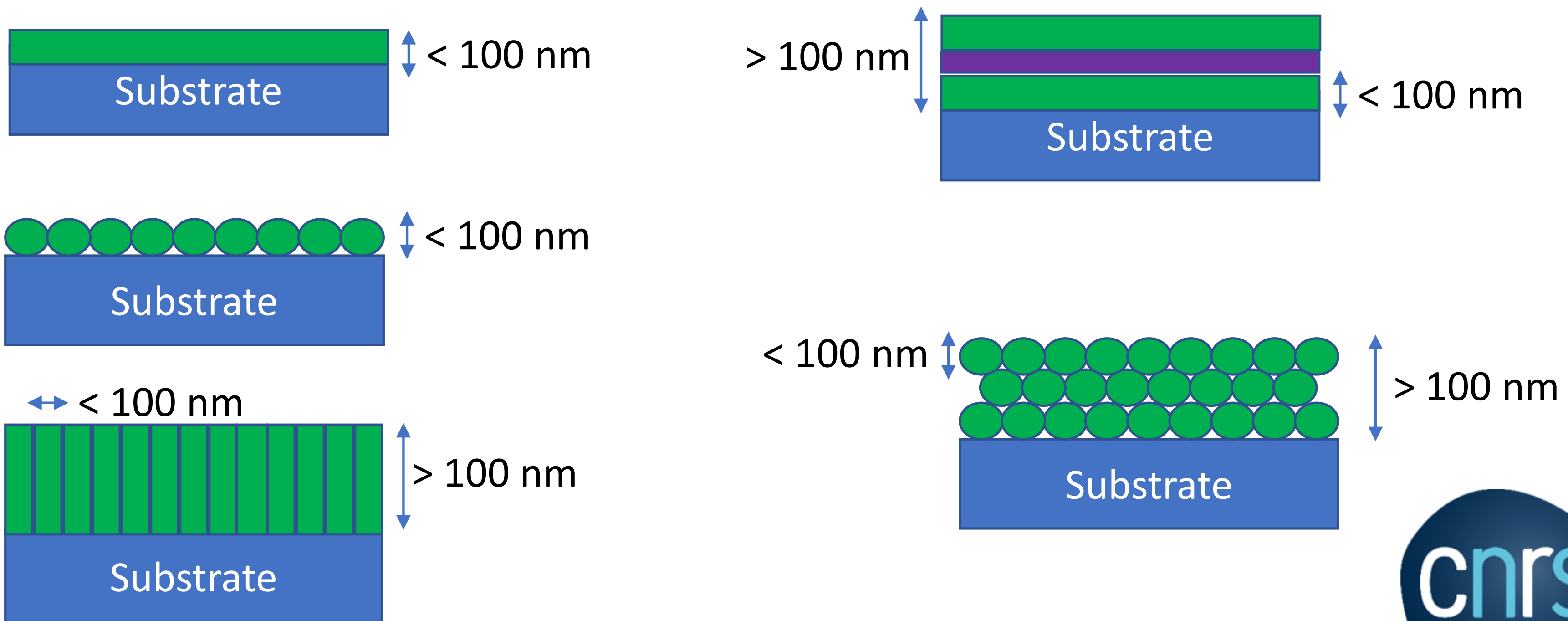




1) Introduction

Definition:

-Nanomaterials (EU definition June 2022, not scientific): They consist of differently shaped small solid particles no larger than one hundred nanometers, or about one thousand times smaller than the thickness of a human hair. As a result, nanomaterials have specific properties and some are exploited by industry and in products.



1) Introduction

These CSD process routes make generally the following possible:

- The synthesis of a broad spectrum of materials (metal, oxides, chaclogenides, carbides, nitrides…),

- The ability to co-synthesise two or more materials simultaneously,

- Coating of one or more materials on to other materials,

- Synthesis of ultra-high purity materials,

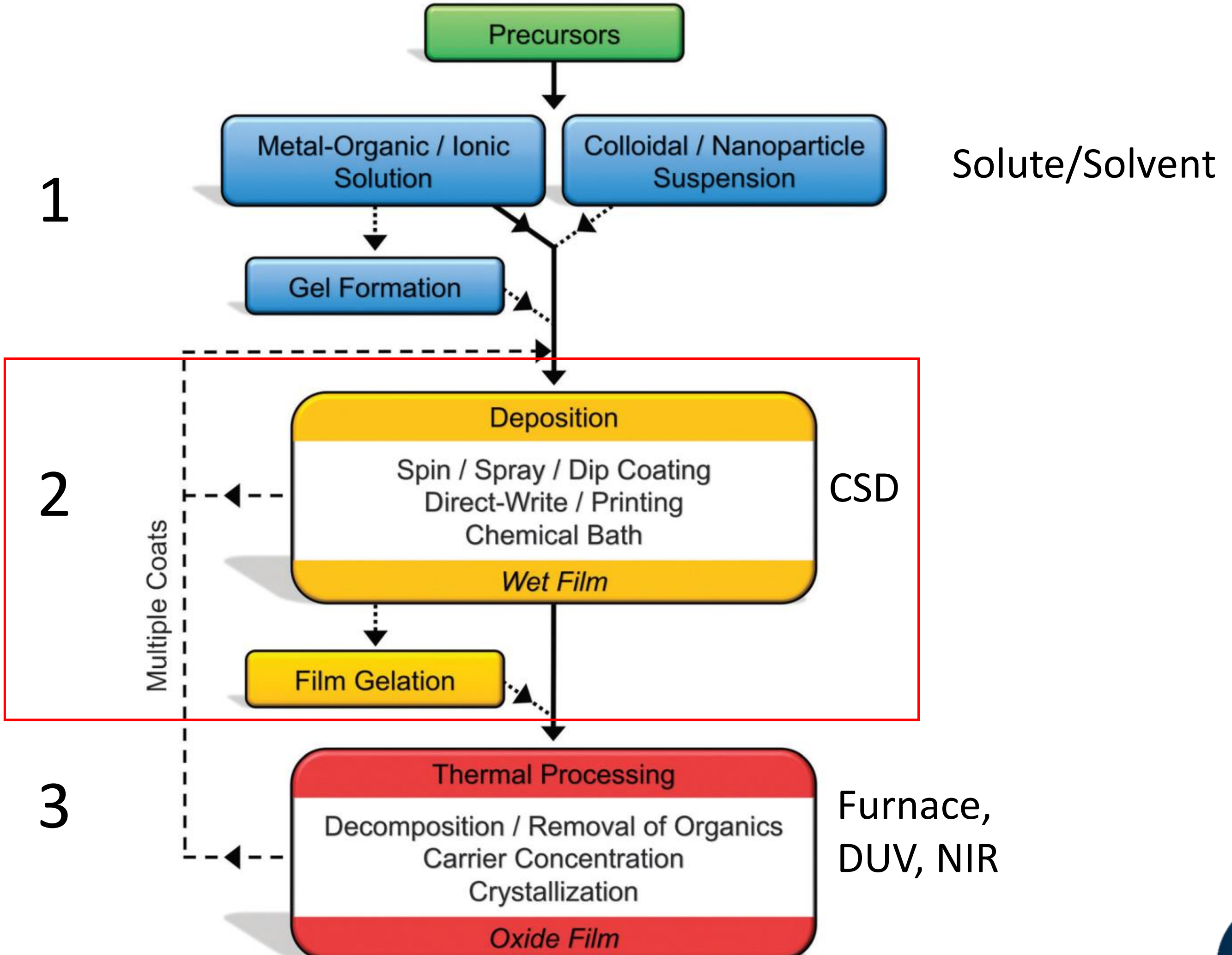
- Very accurate tailoring of the composition even in the early stages of the process,

- Control of the microstructure of the final products,

- Control of the physical, mechanical, and chemical properties of the final products.

1) Introduction

Flow chart of typical solution processing routes



From Chem. Soc. Rev., 2011, **40**, 5406–5441

1) Introduction

Quality of the substrate?

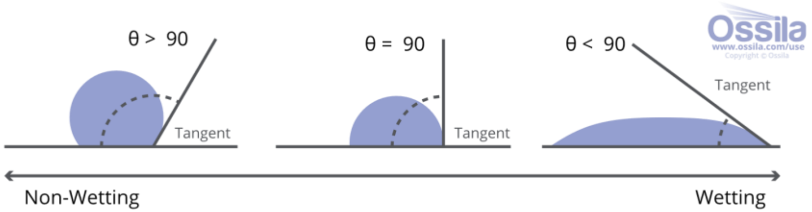
-Substrate Handling (tweezer, glove?)

-Substrate Cleaning
    -Degreasing (Acetone, methanol…)
    -Organic Contaminant Removal (Ozone cleaner, piranha" solution?)
…

-Substrate modification
    -Native oxide removal (HF?)
    -Formation of hydroxide groups (Ozone cleaner)
…

Quality of the solution?

-Viscosity of the solution,
-Wettability of the solvent,



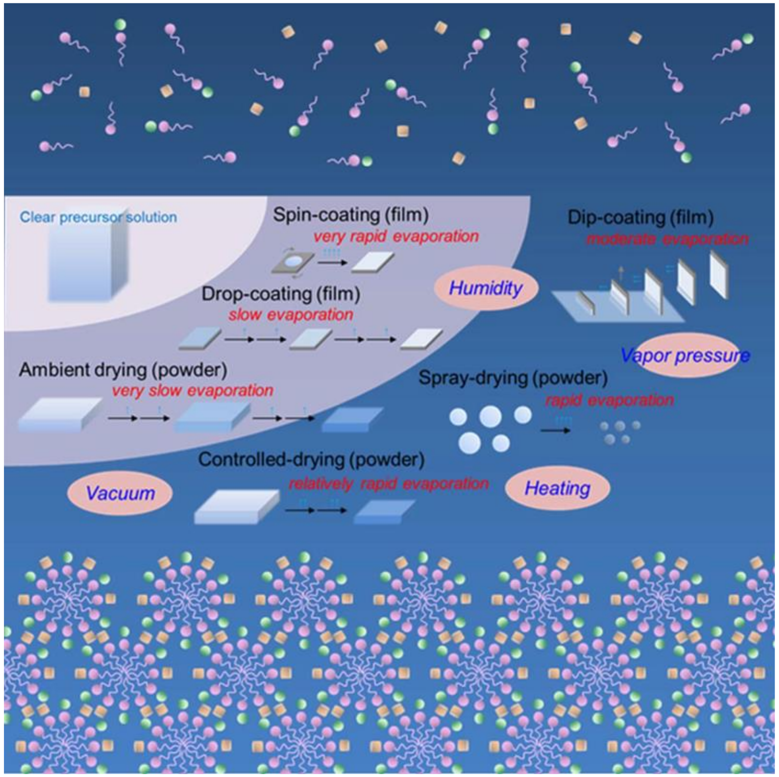
-Boiling point of solvent,
-Solubility of solute,
-Filtration,
-Additional surfactants (EISA)
…

1) Introduction

Evaporation Induced Self-Assembly (EISA)

Film formation + nanostructuration by using self assembly principles

EISA is based on the fact that in coating film formation occurs through evaporation of solvents concentrating the system in non-volatile species, which leads to aggregation and gelation and hence can be also used to induce the formation of functional nanoscopic materials.



T. Kimura, Chem. Rec. 2016, 16, 445–457

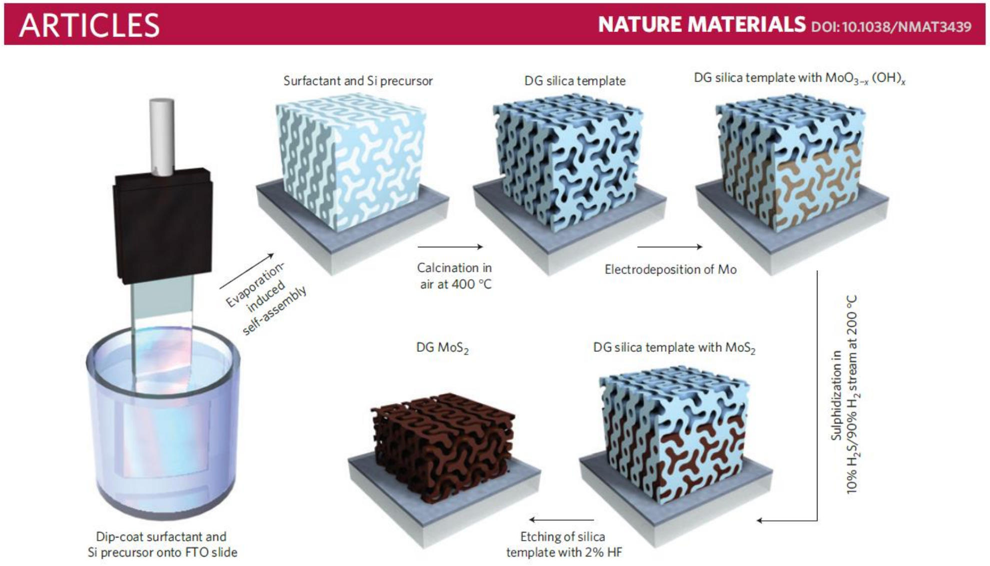


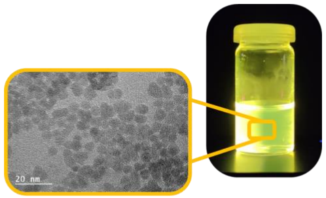
Figure 1 | Synthesis procedure and structural model for mesoporous MoS_2 with a double-gyroid (DG) morphology.

Nature Materials., 2012, 11, 963-969

Fabien Grasset

13th June 2023, EI NANO

1) Introduction

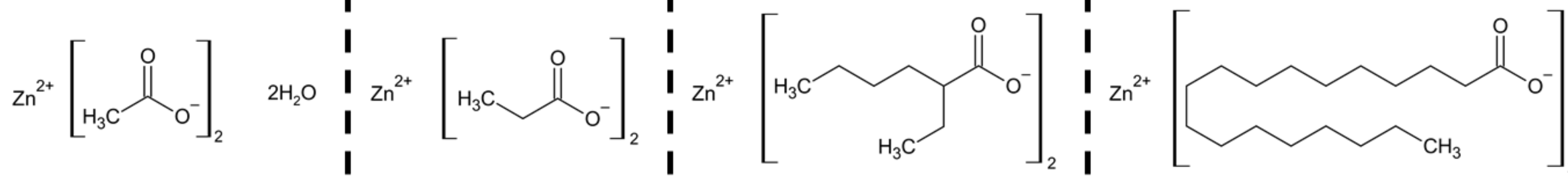


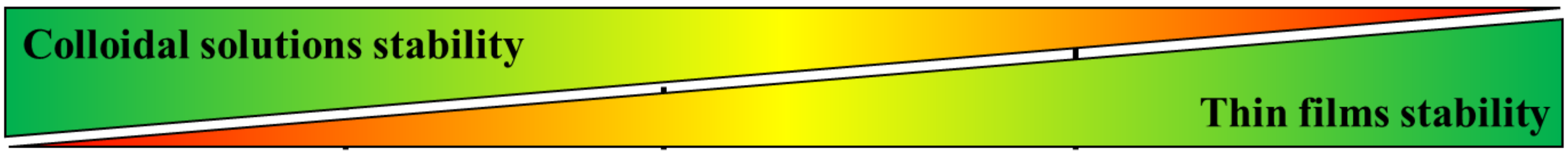
Quality of the film?

Adhesion of ZnO film

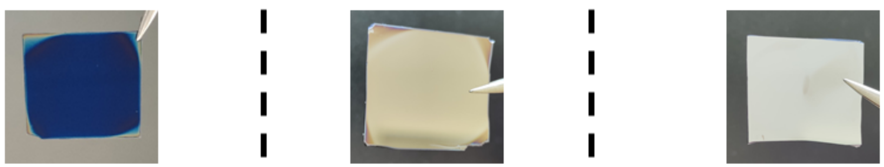
	Acetate	Propionate	2-ethylhexanoate	Stearate

Ligands at the surface





Thin film solubility



Insoluble | Partially soluble | Soluble

Thin film solubility

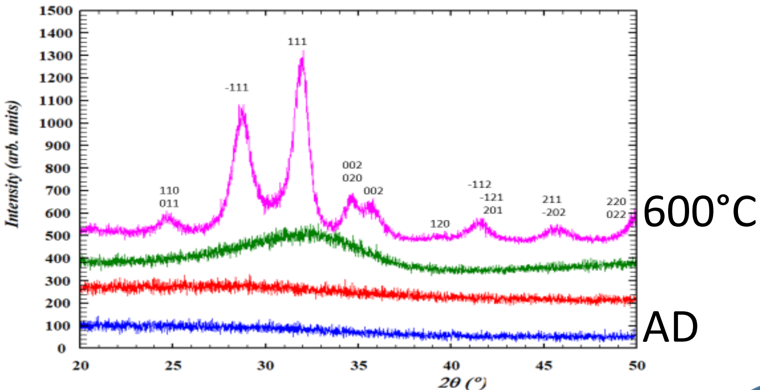
Precipitation in solution

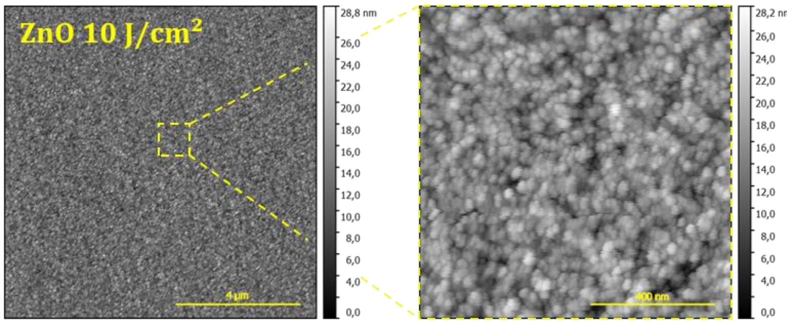
Q. Kirscher, *et al*., Sci. Technol. Adv. Mater., *23*, 044401, 2022

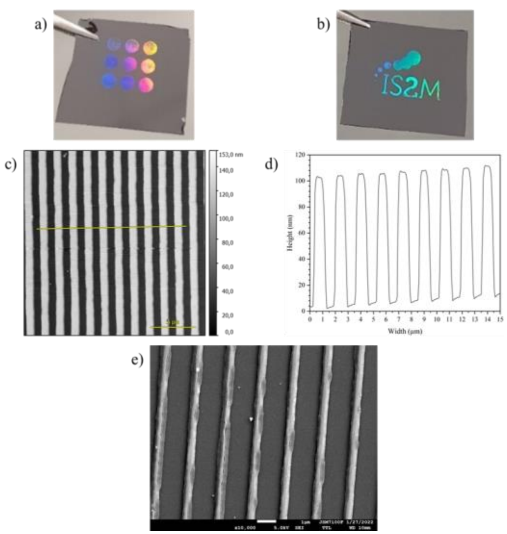
1) Introduction

Thermal processing?

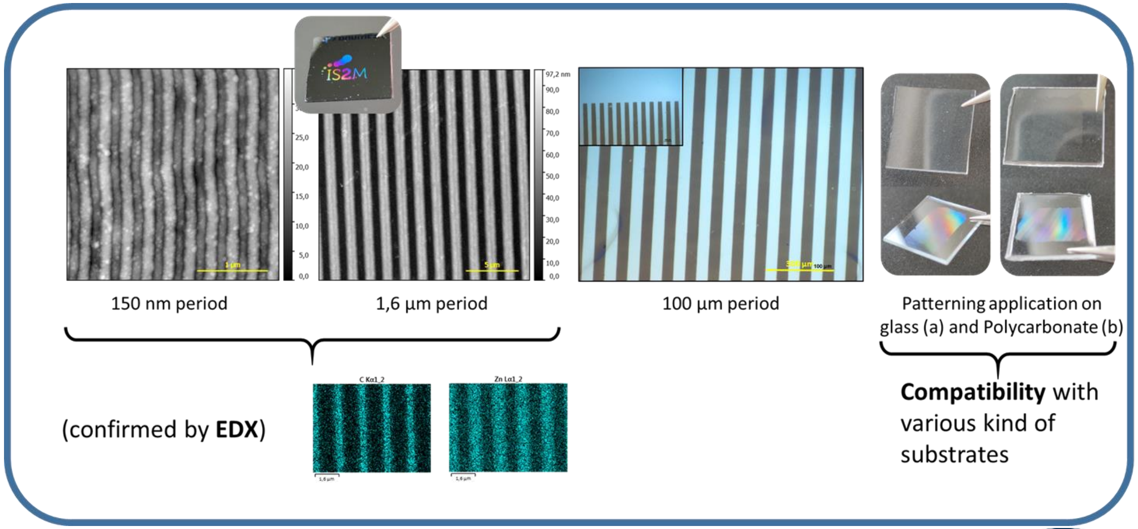
Amorphous versus cristallize







V. Proust, *et al.*, Nanomaterials, 12, 2334, 2022



Q. Kirscher, *et al.*, Sci. Technol. Adv. Mater., *23*, 044401, 2022

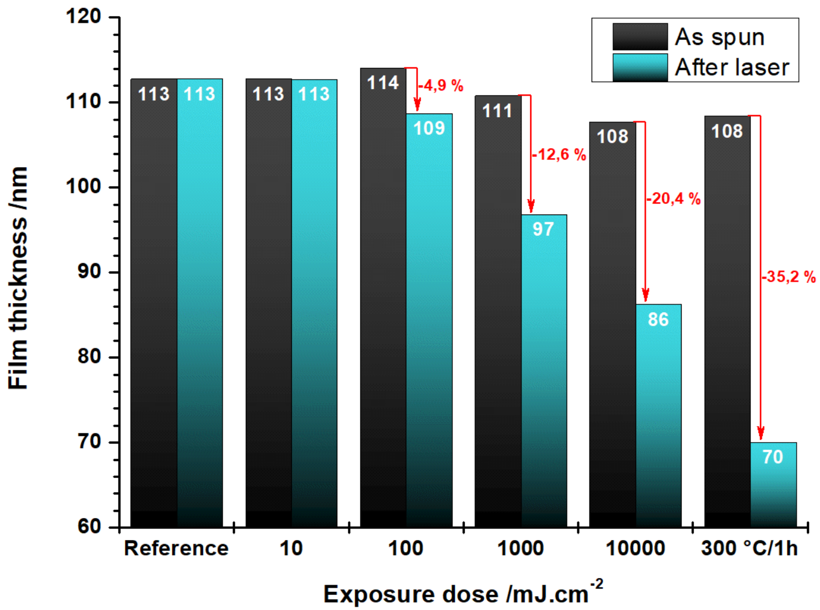
Fabien Grasset

13th June 2023, EI NANO

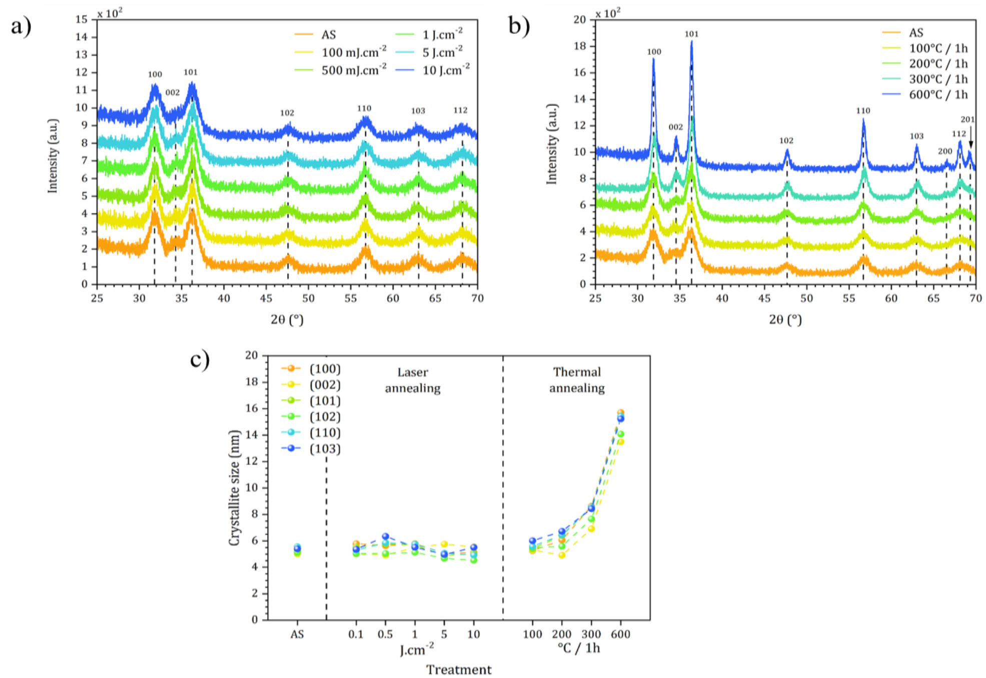
1) Introduction

“Thermal” processing?
Furnace, laser…

Shrinkage of the film



Effect on the cristallite size

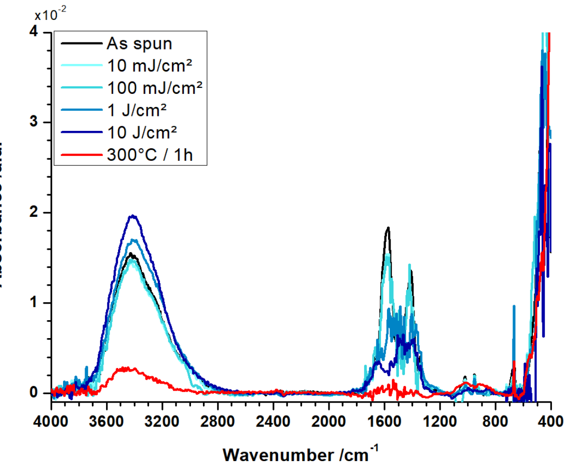


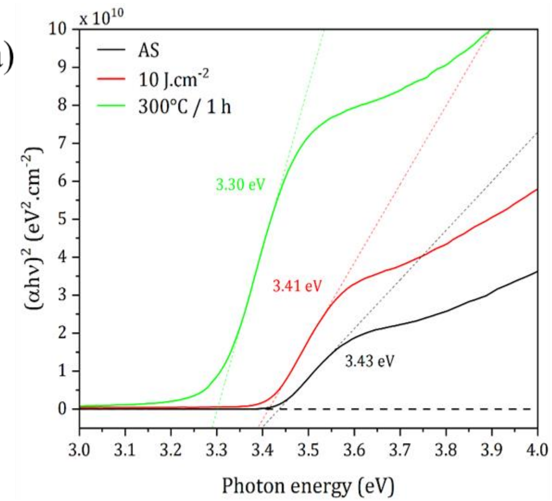
Q. Kirscher, *et al*., Sci. Technol. Adv. Mater., *23*, 044401, 2022

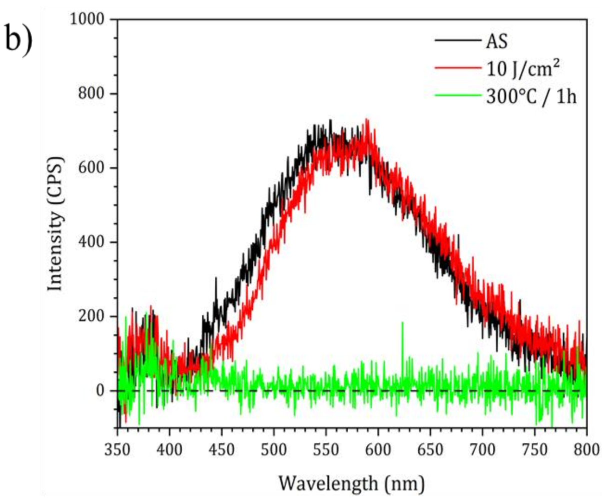
1) Introduction

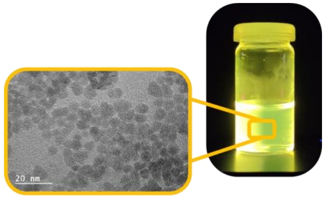
“Thermal” processing?

Impact on the physical properties!
How to keep the properties of « Nano »

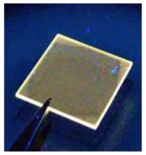




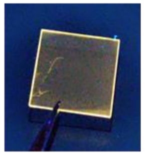




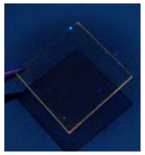
c)



As spun



10 J/cm²



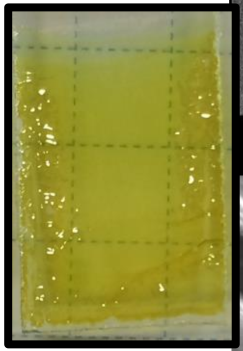
300°C / 1h

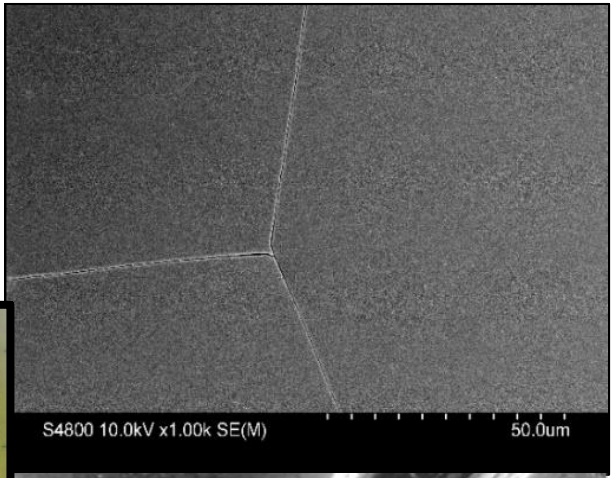
Q. Kirscher, *et al.*, Sci. Technol. Adv. Mater., *23*, 044401, 2022

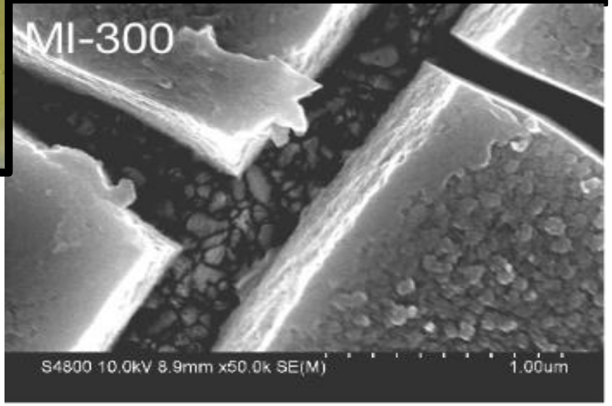
1) Introduction

Quality of the film?

Cracking





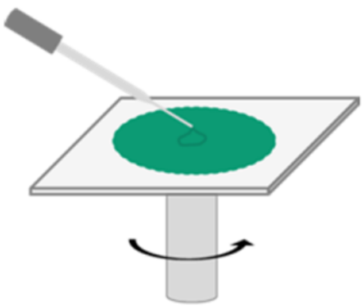


-Thermal expansion mismatch
-Mechanical stresses (compression, tension)
…

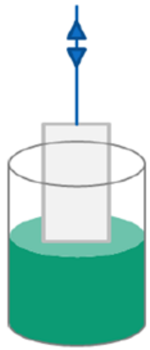
-Increase with the film thickness

Solutions:
-Additional binders (polymers, metallic salt…)
-Additional capping layer (PDMS)
-Multi-step deposition

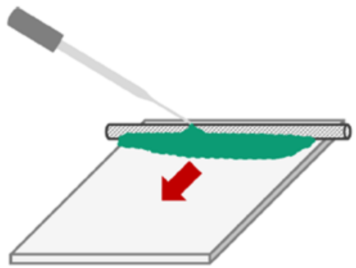
1) Introduction



Spin coating

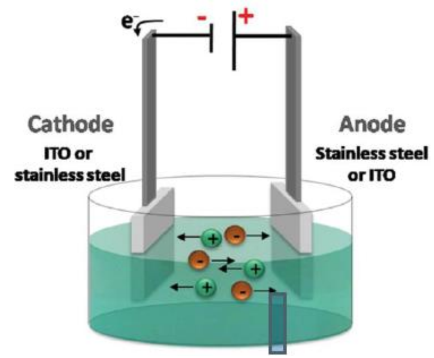


Dip coating



Mayer bar coating

Spray coating



Electrophoretic

Outline

1) Introduction

2) Spin-Coating

3) Dip-Coating

4) Mayer bare coating

5) Spray-Coating

6) EPD

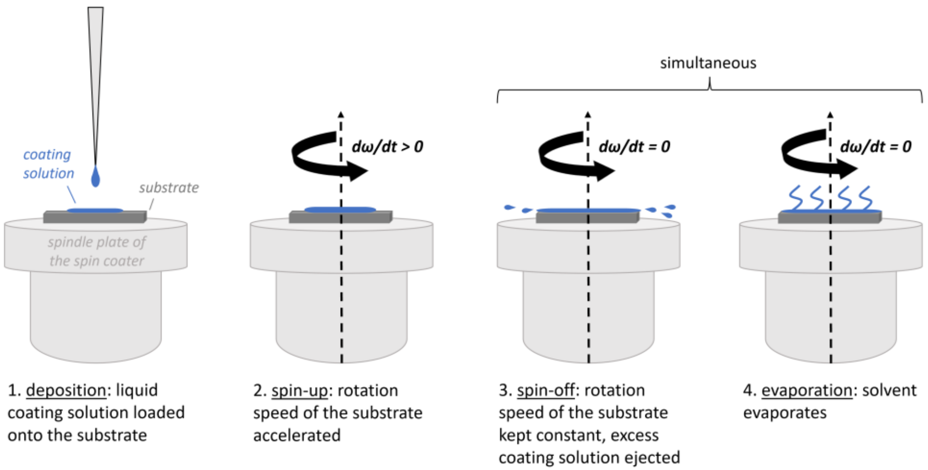
7) Conclusion

2) Spin-Coating

Spin coating generally involves the application of a thin film (from a few nm to a few µm) uniformly across the surface of a rotating substrate by casting a solution of the desired material. A machine used for spin coating is called a spin coater, or simply spinner.

3 important steps:

1-Dispense of the coating solution
2-fluid flow dominated thinning
3-Solvent evaporation and coating set

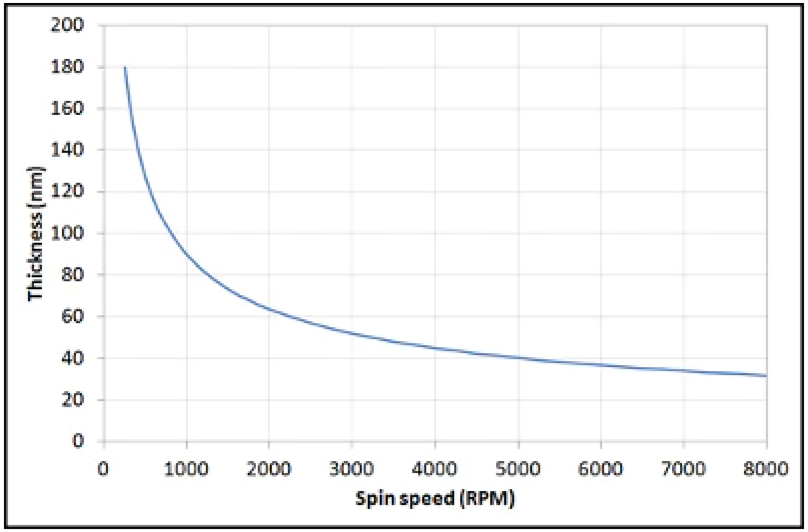


https://www.ossila.com

2) Spin-Coating

Spin Coating Thickness Equation

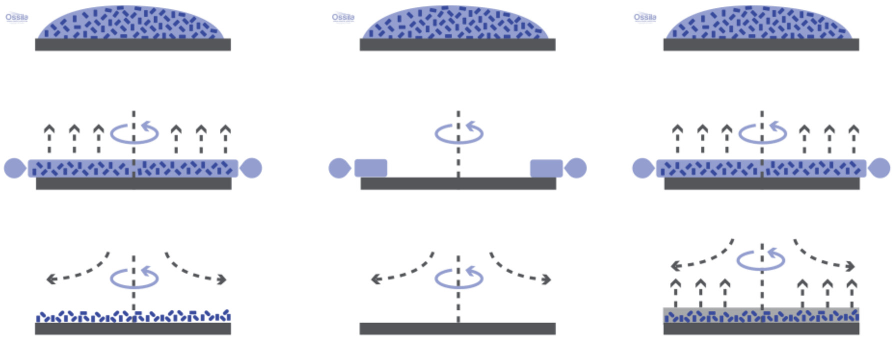
$$h_f \propto \frac{1}{\sqrt{\omega}}$$



h_f = final film thickness
ω = angular velocity/spin speed

The thickness of a film will mainly depend upon:

- The solute concentration
- The solvent evaporation rate (which in turn depends upon the solvent viscosity, vapor pressure, temperature and local humidity)

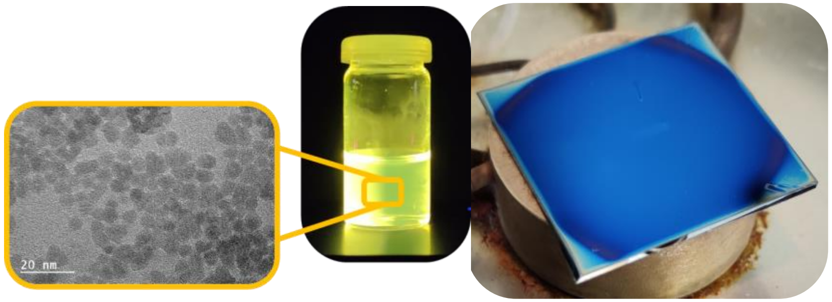


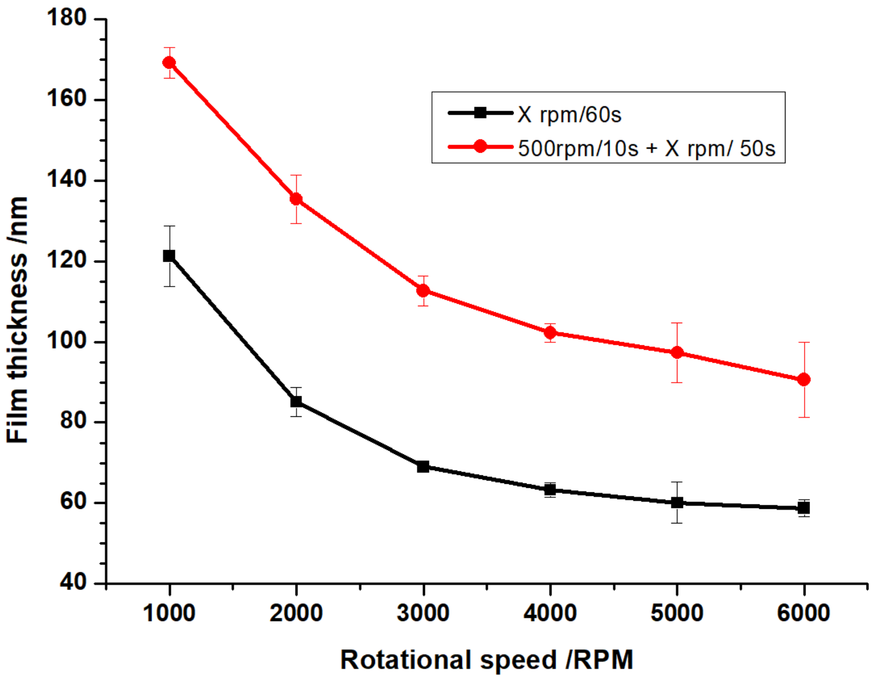
So for these reasons spin thickness curves for new solution are most commonly determined empirically…

-Emslie, Bonner, and Peck Model
-Meyerhofer Model

2) Spin-Coating

Spin Coating Thickness Equation

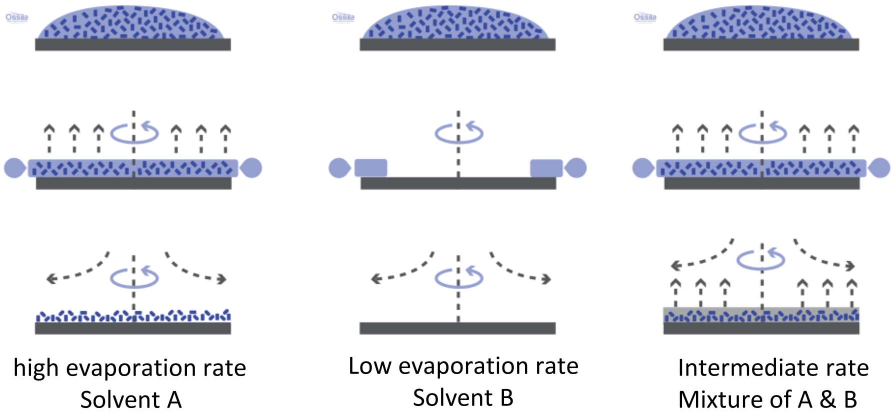




Q. Kirscher, *et al*., Sci. Technol. Adv. Mater., *23*, 044401, 2022

The thickness of a film will mainly depend upon:

- The solute concentration
- The solvent evaporation rate (which in turn depends upon the solvent viscosity, vapor pressure, temperature and local humidity)



So for these reasons spin thickness curves for new solution are most commonly determined empirically…

-Emslie, Bonner, and Peck Model
-Meyerhofer Model

2) Spin-Coating

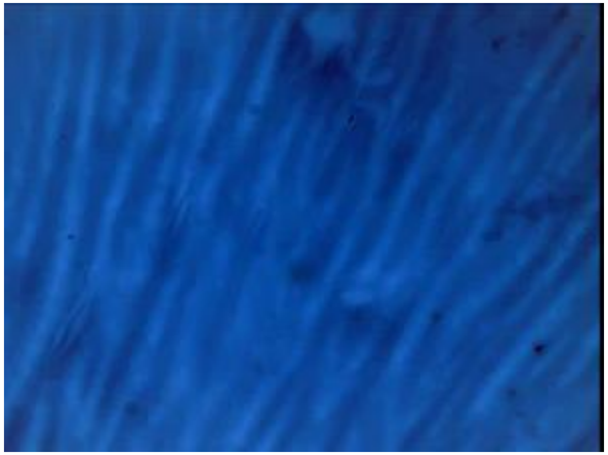
Current difficulties!!!

Solutions with poor solute's solubility

-Very low solute concentration => very thin film => Low spin speed and static deposition

-Additional components, co-solvent
-Heating, sonication…

Solutions with extreme volatility (high or low)



Marangoni instabilities

highly-volatile solutions:
-Additional components, co-solvent
-Low spin speed and static deposition

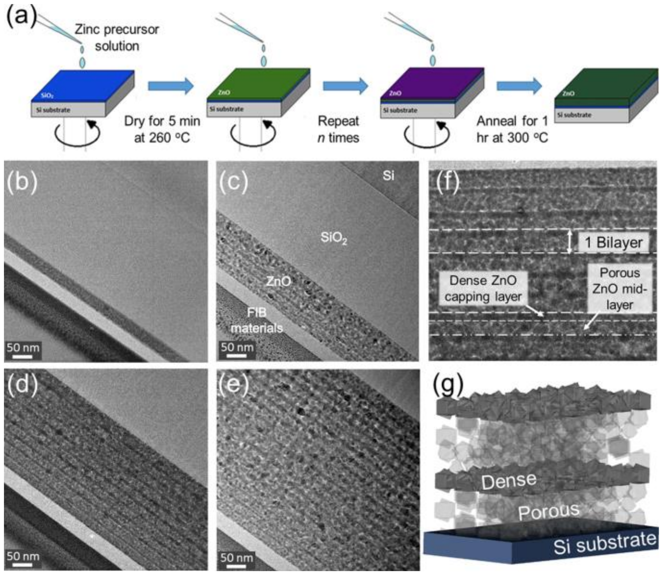
low volatility solutions:
⇒ long drying times => very thin films
-edge effects (thicker film around the edges compared to the center)

Poorly-wetting solutions

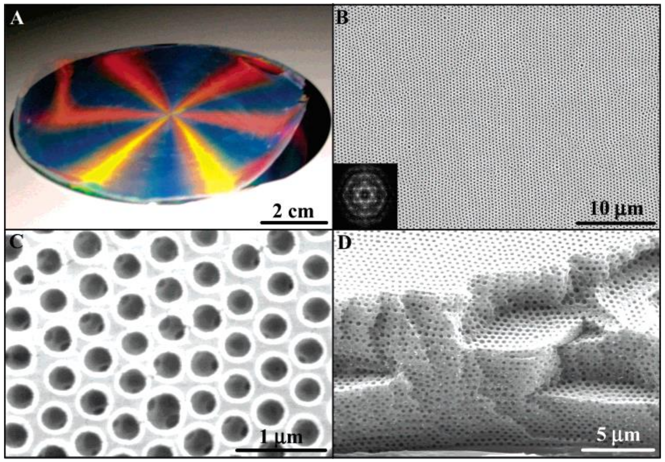
-Ozone cleaner
-Surface tension modifiers: surfactants

2) Spin-Coating

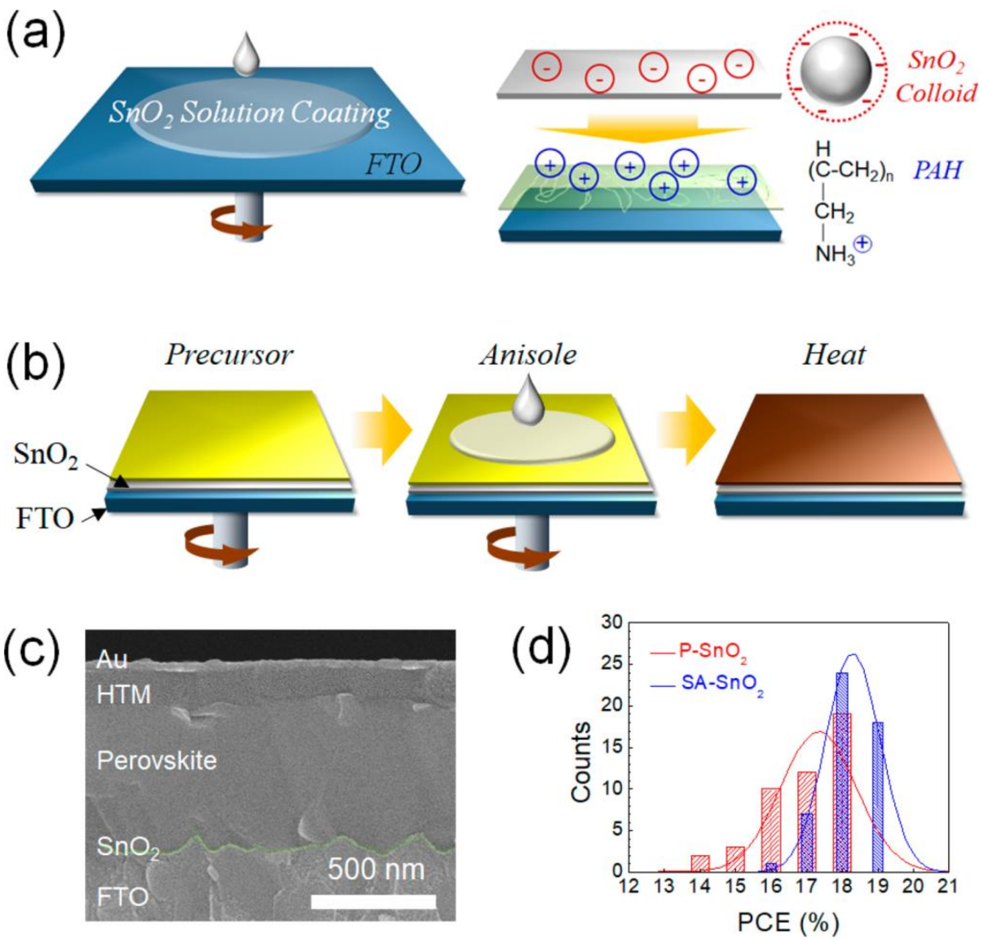
Adapted for a lot of examples!!!



https://doi.org/10.1116/1.5001758



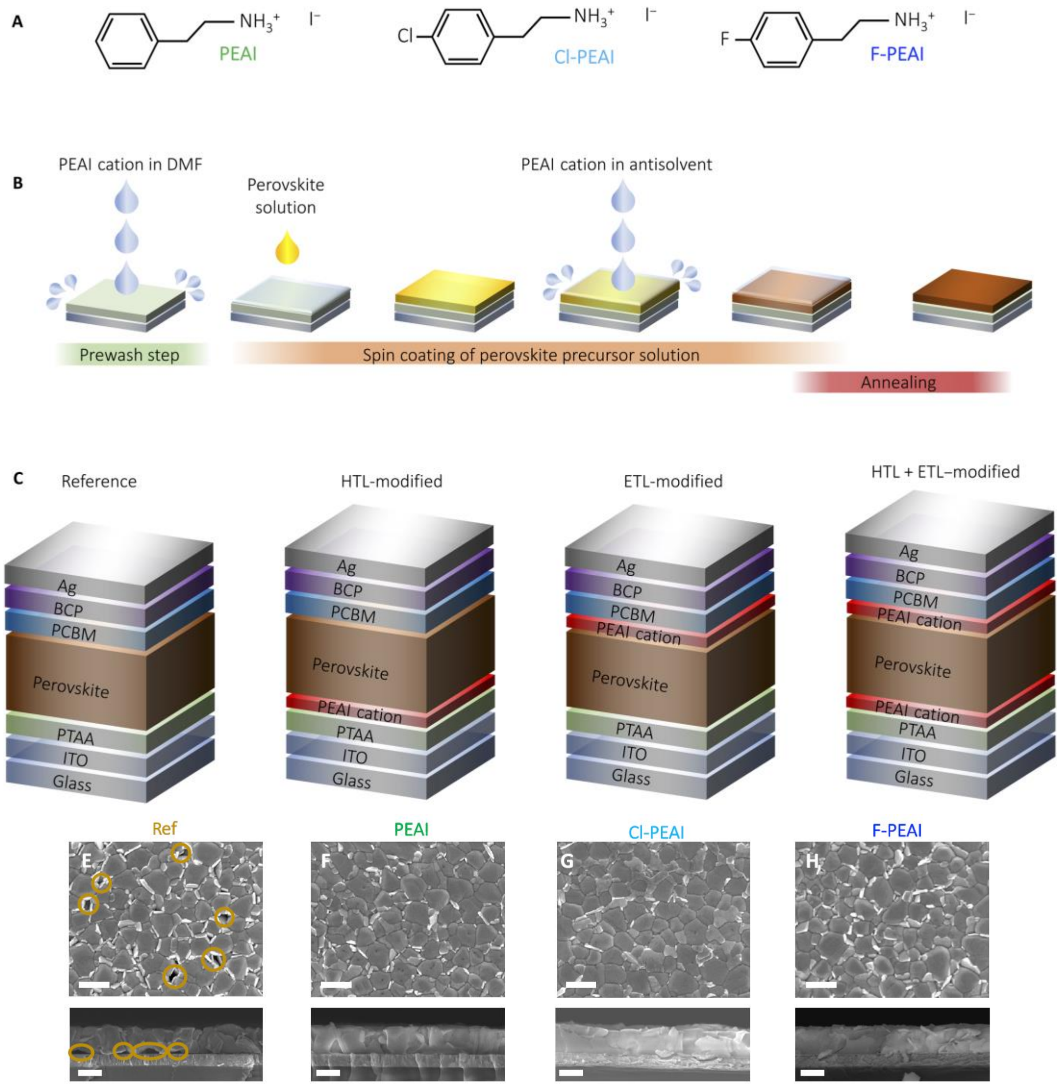
Self-standing macroporous polymer replica after removal of silica spheres
J. Am. Chem. Soc., 2004, 126, 13778



DOI: 10.1021/acsenergylett.9b00953
ACS Energy Lett. 2019, 4, 1845−1851

2) Spin-Coating

Adapted for a lot of examples!!!



Degani *et al.*, *Sci. Adv.* **7**, eabj7930 (2021)

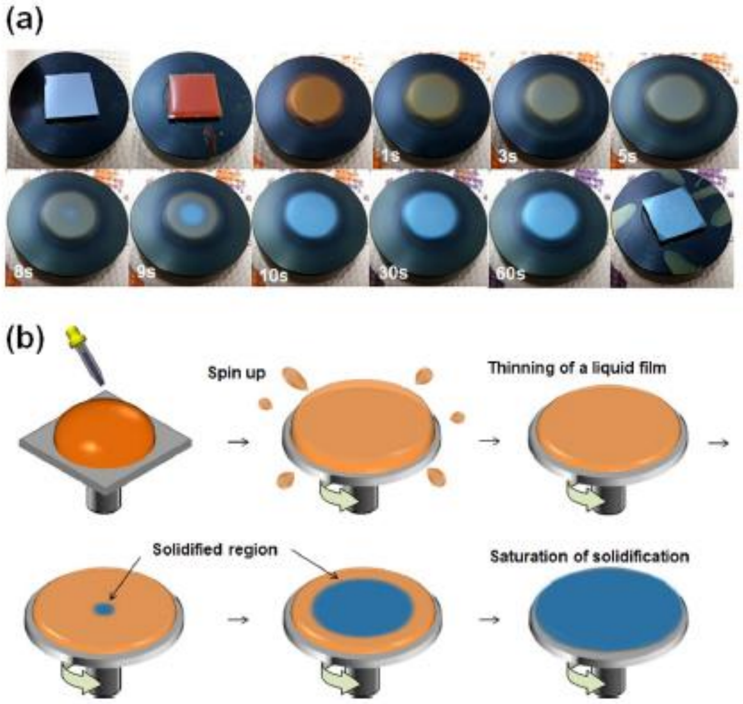
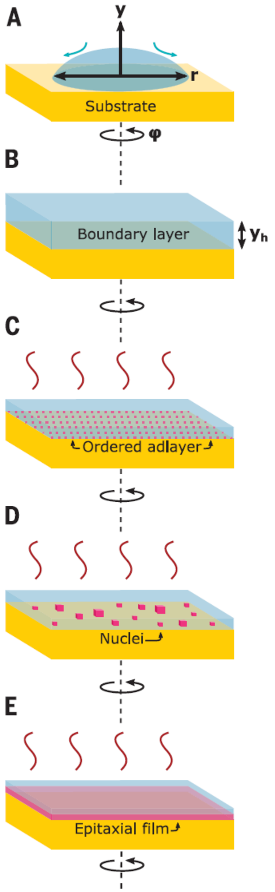


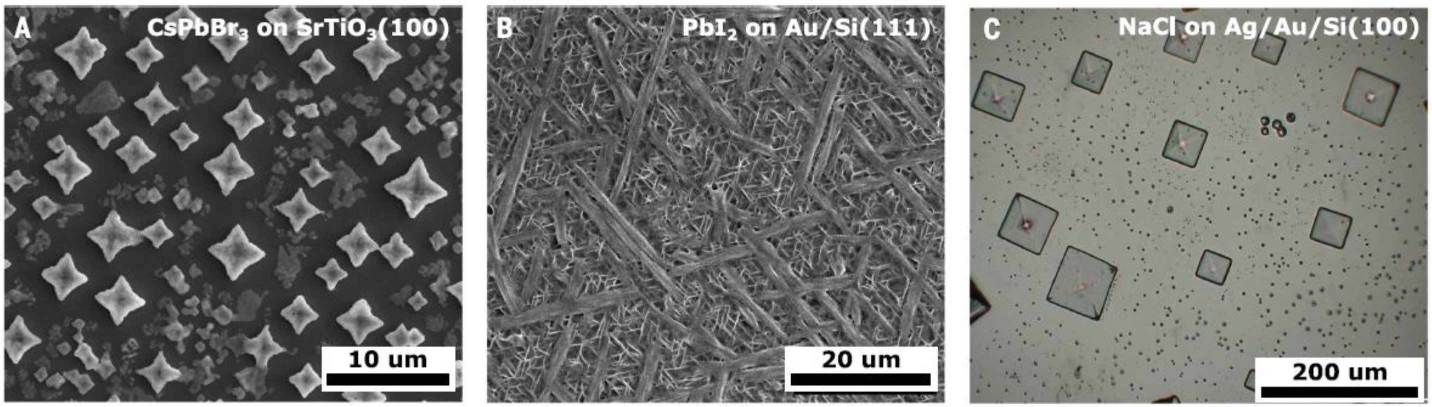
Figure 8. Optical monitoring during spin coating and its schematic illustration. (a) Videomicroscopy images of the spin-coating process at specific times after initiation, where the P3HT solution consisted of 1 wt% P3HT in chlorobenzene solvent. (b) Schematic diagram showing the spin-coating steps.

2) Spin-Coating

Adapted for a lot of examples!!!

Spin coating epitaxial films





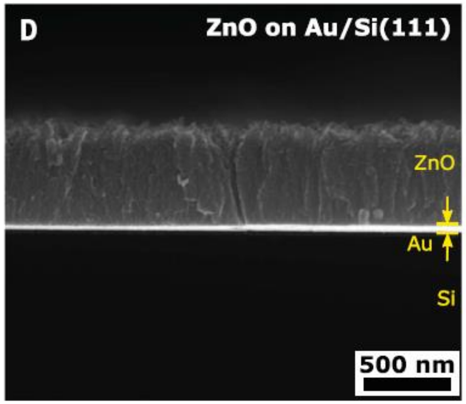


Fig. 2. Morphology of spin-coated materials. (**A** and **B**) SEM micrograph of $CsPbBr_3$ on $SrTiO_3(100)$ (A) and PbI_2 on Au/Si(111) (B). (**C**) Optical micrograph of NaCl on Ag/Au/Si(100). (**D**) SEM cross section of ZnO on Au/Si(111).

Kelso *et al.*, *Science* **364**, 166–169 (2019)

2) Spin-Coating

The main advantages:

•Simplicity and very short process,
•Thin and uniform coating,
•Macroscopic and nano length scales,
•(Very) Low cost and energy process.

The main disadvantages:

•Single substrate batch,
•Small substrate (?),
•Wasted material (big issue for large-scale manufacturing)

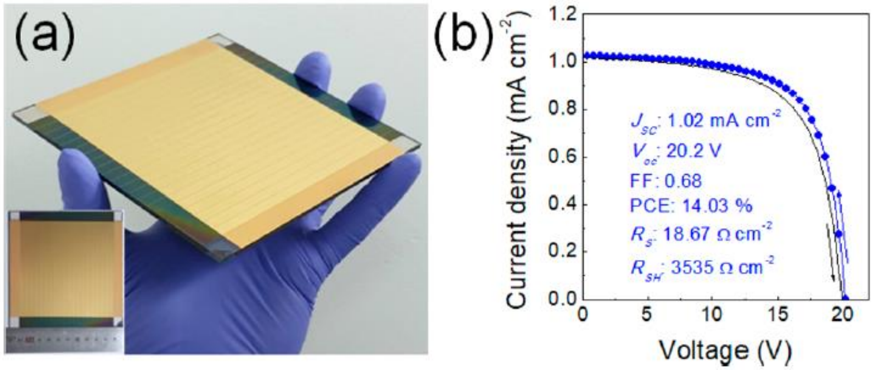


Figure 5. (a) Photograph and (b) current density−voltage curve of the 10 cm × 10 cm PSM (series connection of 20 cells)

DOI: 10.1021/acsenergylett.9b00953
ACS Energy Lett. 2019, 4, 1845−1851

Research and rapid prototyping

Outline

1) Introduction

2) Spin-Coating

3) Dip-Coating

4) Mayer bare coating

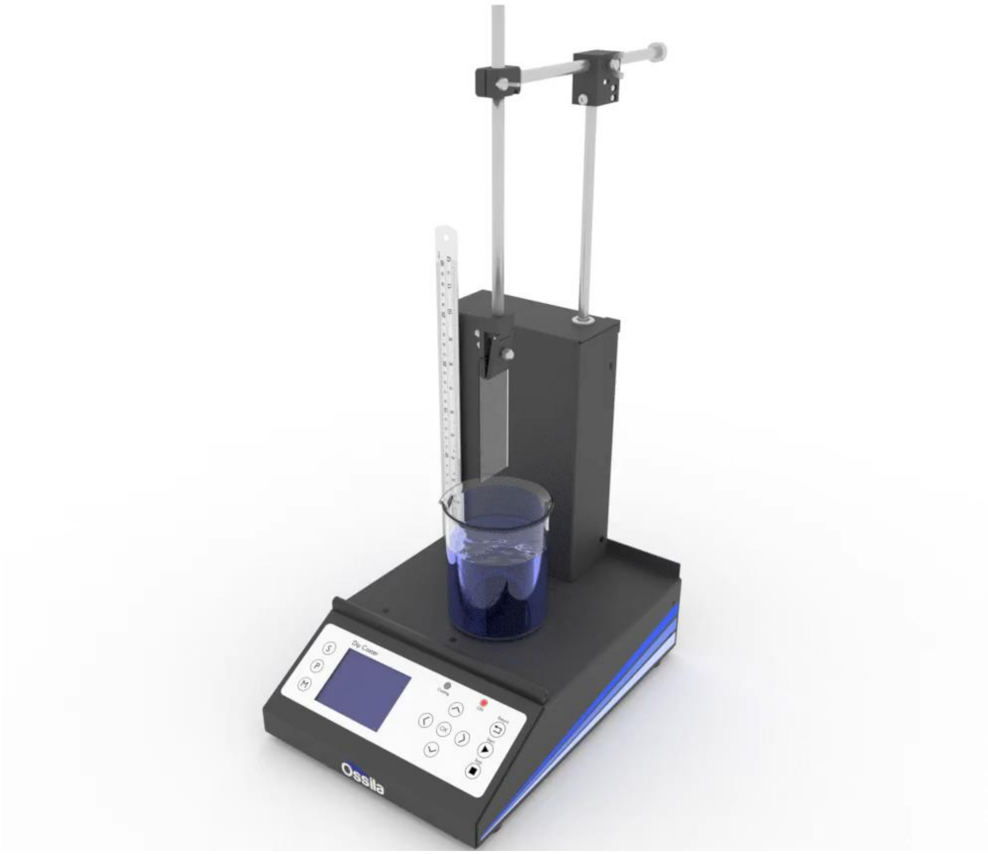
5) Spray-Coating

6) EPD

7) Conclusion

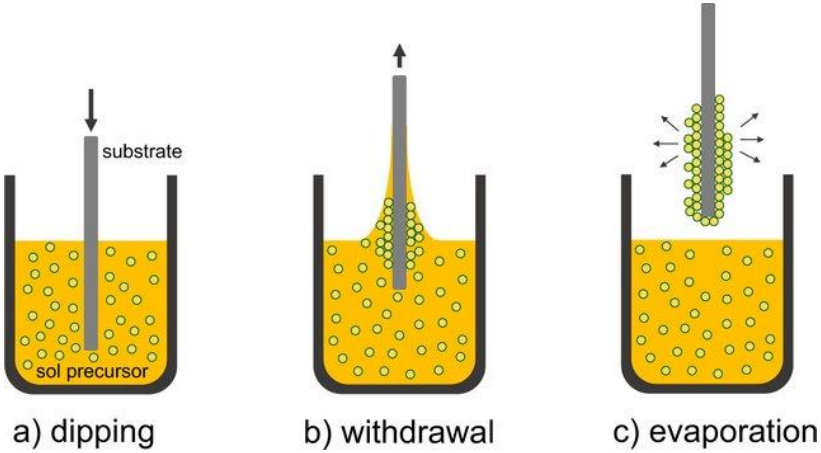
3) Dip-Coating

Dip coating is a process by which substrate material is submerged in coating solution, then taken out and allowed to drip dry.



3 important steps:

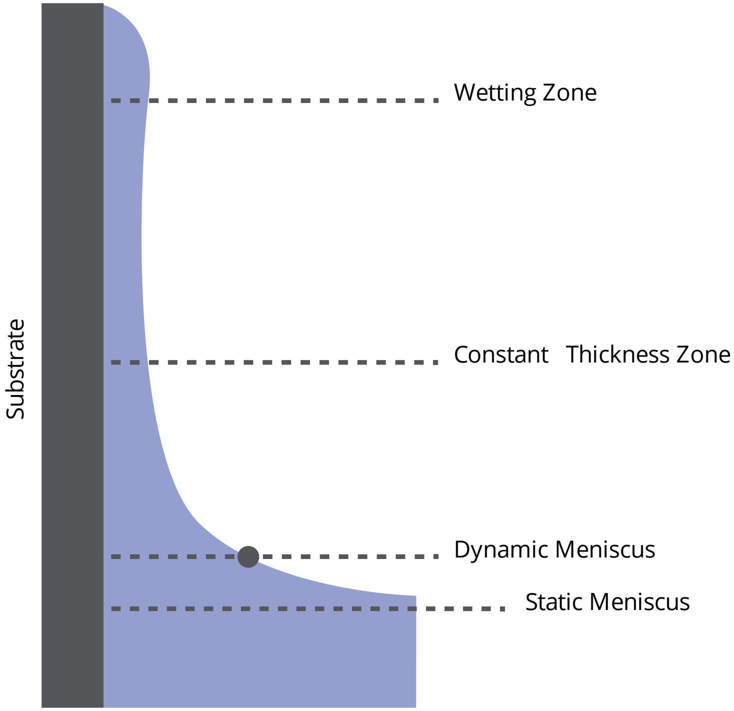
1-Immersion and dwell time
2-Deposition and drainage
3-Evaporation



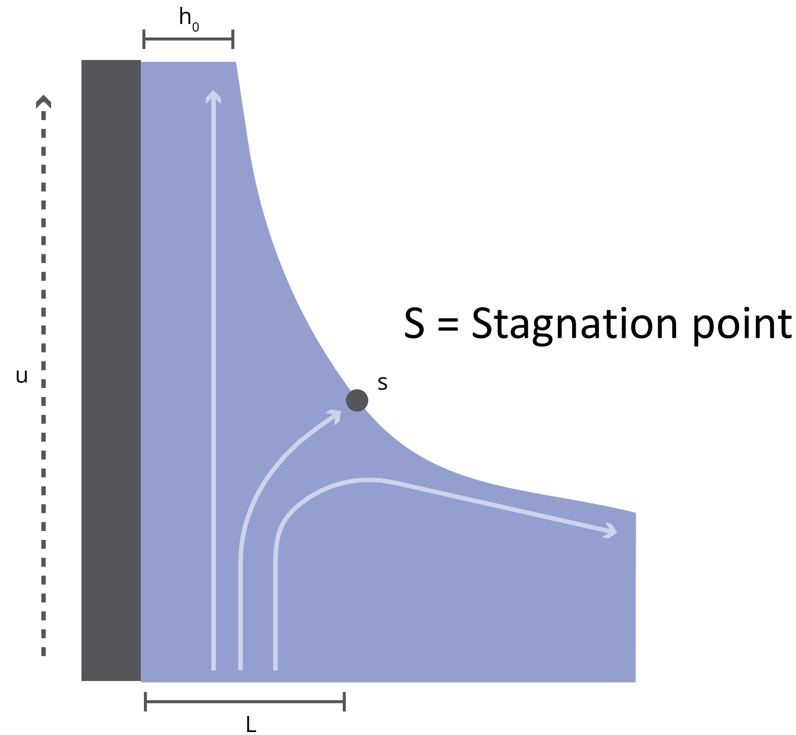
DOI: 10.1007/s10971-021-05628-5

It is important to leave the substrate in the ink for a period of 30-60 seconds during immersion. This allows it to reach thermal equilibrium with the ink.

3) Dip-Coating

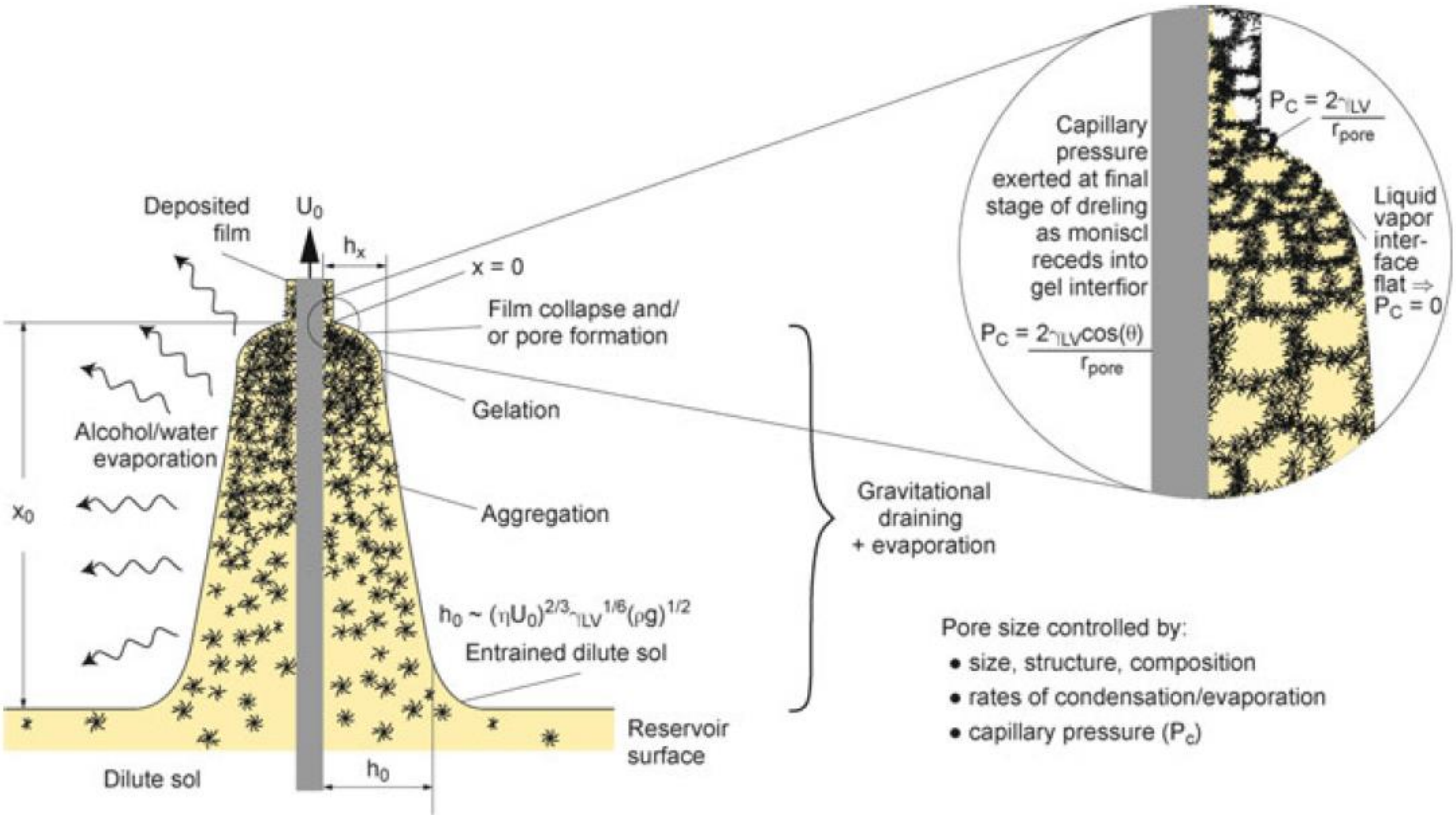


Draining regime



-Static meniscus: where the shape of the meniscus is determined by the balance of the hydrostatic and capillary pressures.
-Dynamic meniscus: which occurs around the stagnation point. The stagnation point is where the entraining forces and draining forces are in equilibrium.
-Constant thickness zone: where the wet film has reached a given thickness (h_0).
-Wetting zone: which is the region where the wet film begins.

3) Dip-Coating



η is the liquid viscosity

ρ is the liquid density

P_c is the capillary pressure

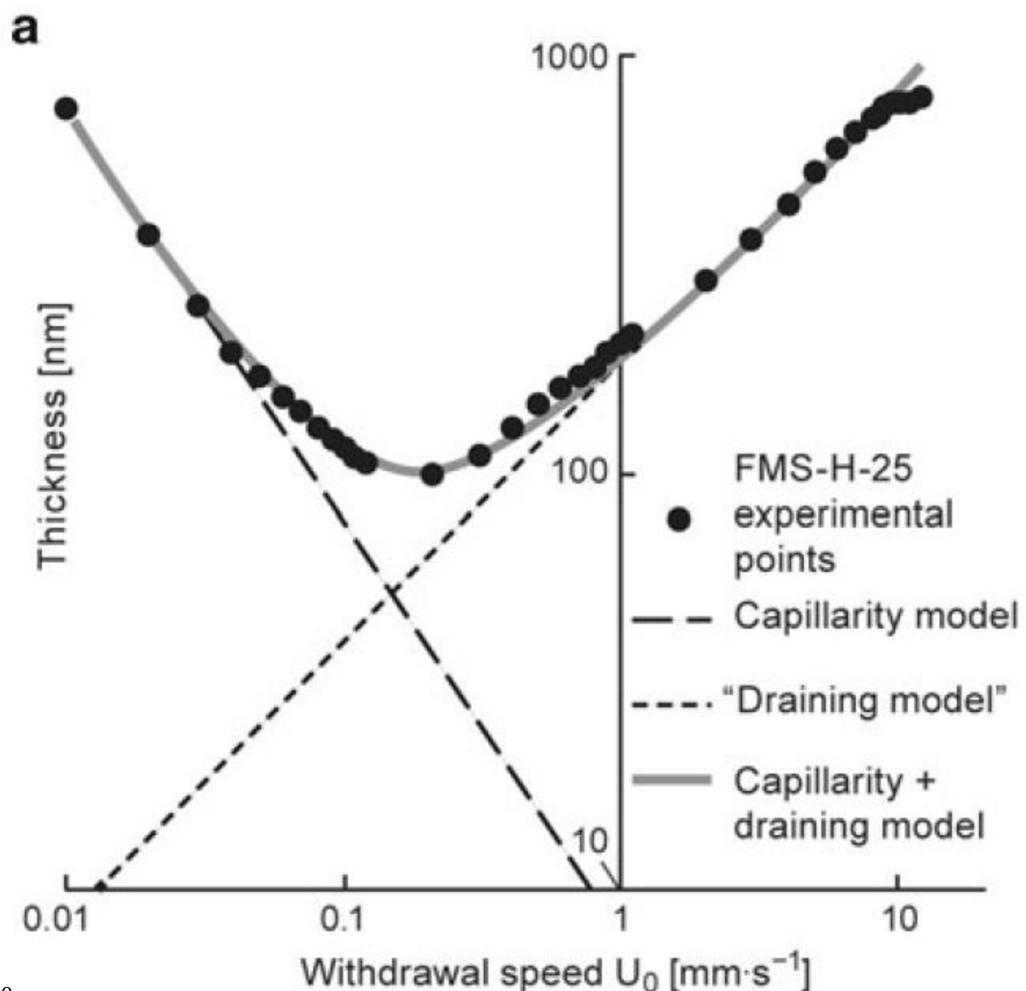
γ_{LV} is the liquid-vapor surface tension

g gravity

3) Dip-Coating

Dependence of film thickness changes on withdrawal speed.

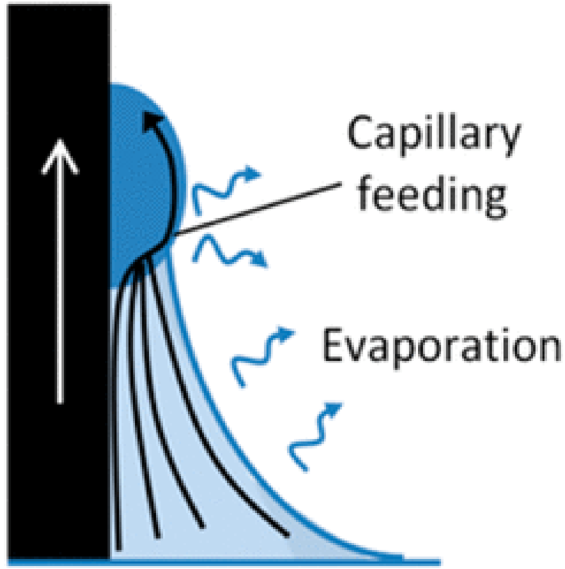
Units are arbitrary as this graph only shows a general trend. Other factors, such as liquid viscosity, can affect the actual film thickness.



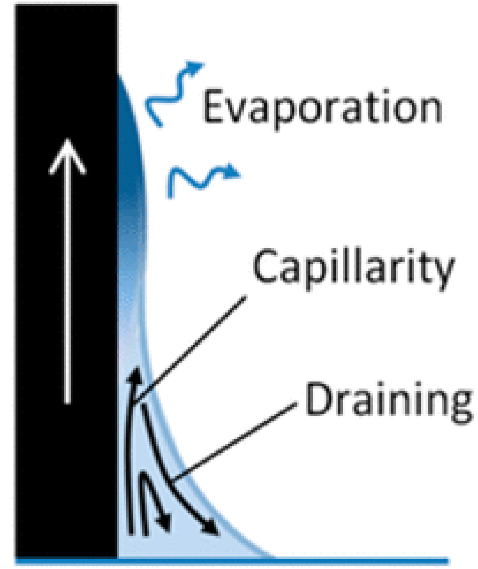
D. Grosso et al., J. Phys. Chem. C, 114, 17, 2010

3) Dip-Coating

E. Bindini et al., J. Phys. Chem. C 2017, 121, 14572−14580



Capillarity regime



Draining regime

Capillarity regime:
Thicker films can be obtained with highly diluted solutions at ultralow withdrawal speed.

Berre equation

$$h = k_i \frac{E}{L} U^{-1}$$

E: evaporation rate
U: withdrawal speed
L: width of the film

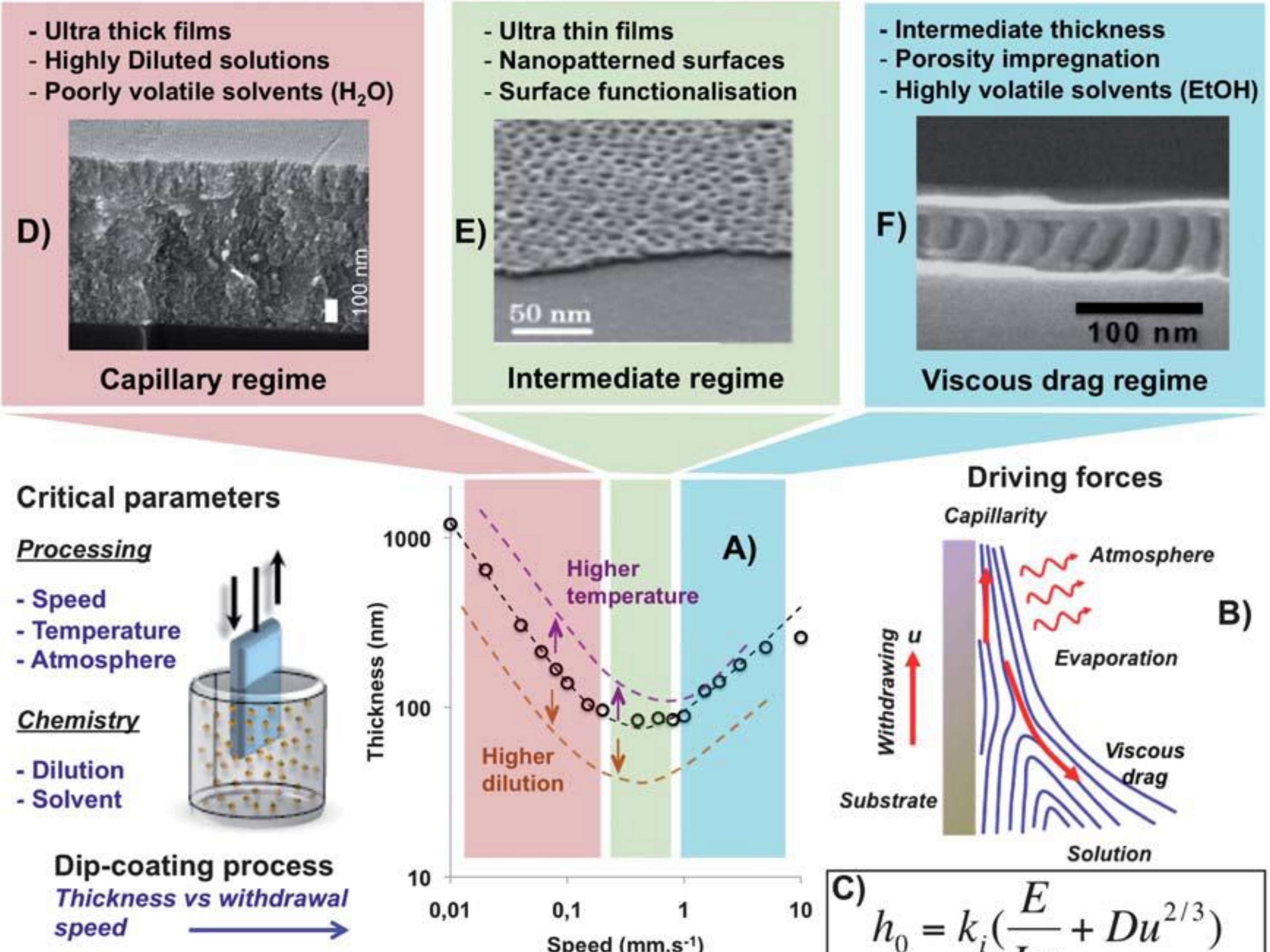
Draining regime:
Usually applied withdrawal speeds in the range of ~1–10 mm/s

Landau-Levich Model

$$h = \frac{0.94\,(\eta U)^{2/3}}{\gamma_{LV}{}^{1/6}(\rho g)^{1/2}}$$

(Newtonian fluid and non-evaporating fluid)

3) Dip-Coating



$$h_0 = k_i\left(\frac{E}{Lu} + Du^{2/3}\right)$$

J. Mater. Chem., 2011, 21, 17033–17038

3) Dip-Coating

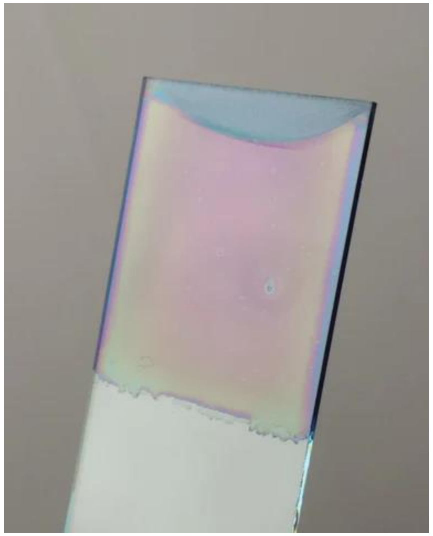
Current difficulties!!!

Stripe defects

Due to:
-Low withdrawal speed (capillary region)
-Low solute concentration

⇒ increase the withdrawal speed or reduce the ambient temperature.
⇒ increase the concentration

Visible particles, pinholes and craters



Due to:
-Dust or contamination on the substrate before coating
-Aggregation or crystallization of the solute
-Evaporation cooling effects

=> Cleaning, additional components, co-solvent, heating, sonication, cool down…

Partial or inhomogeneous coating of the substrate

-Insufficient wetting
-Turbulent airflow during drying
-Inconsistent withdrawal speed
-Meniscus height issues

Running (Curtaining)

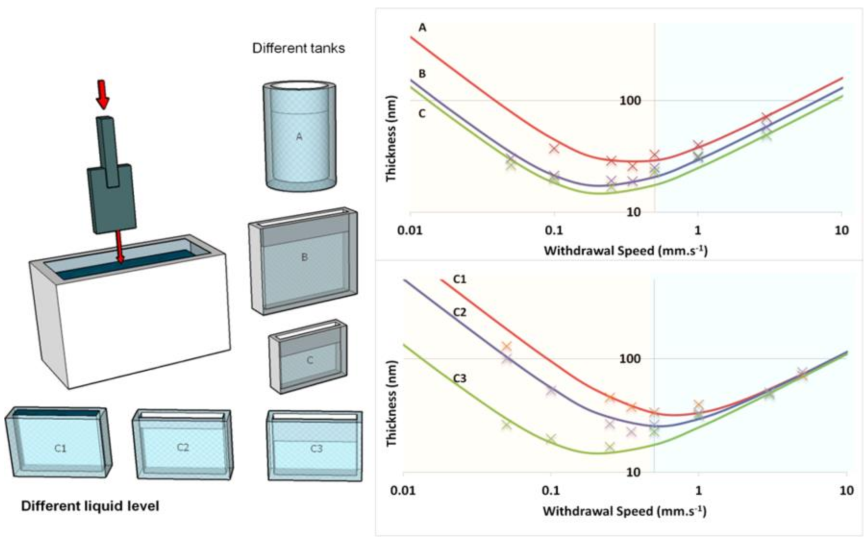
Due to:
-Long drying times caused by large wet film thicknesses
-Low viscosity of solvent

=>Increase the viscosity of the solution, increase the temperature

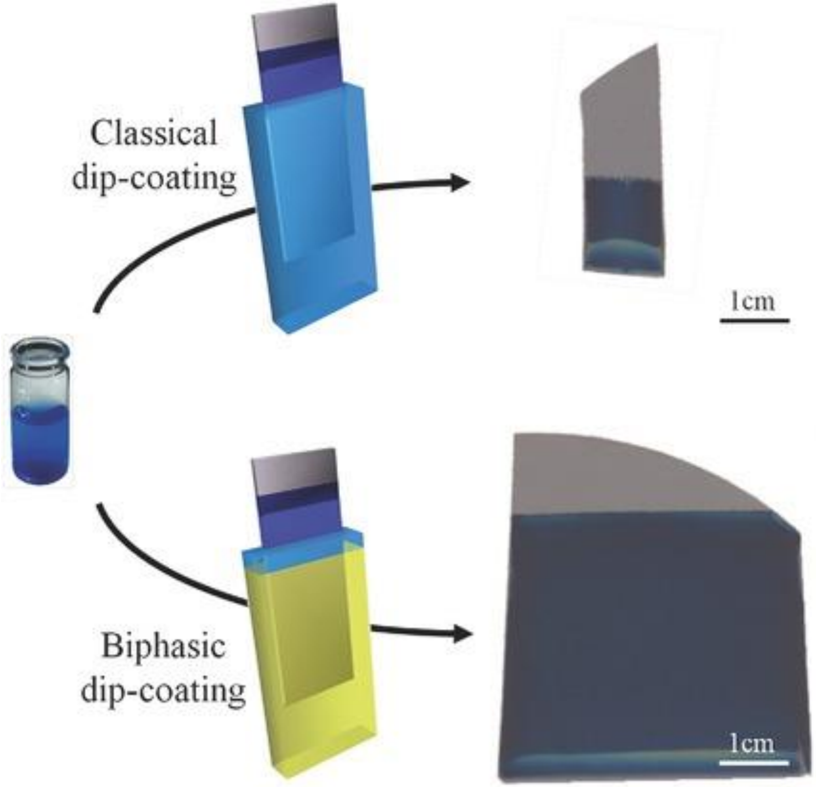
3) Dip-Coating

Capillarity regime

The role of the container?



E. Bindini et al., J. Phys. Chem. C 2017, 121, 14572−14580



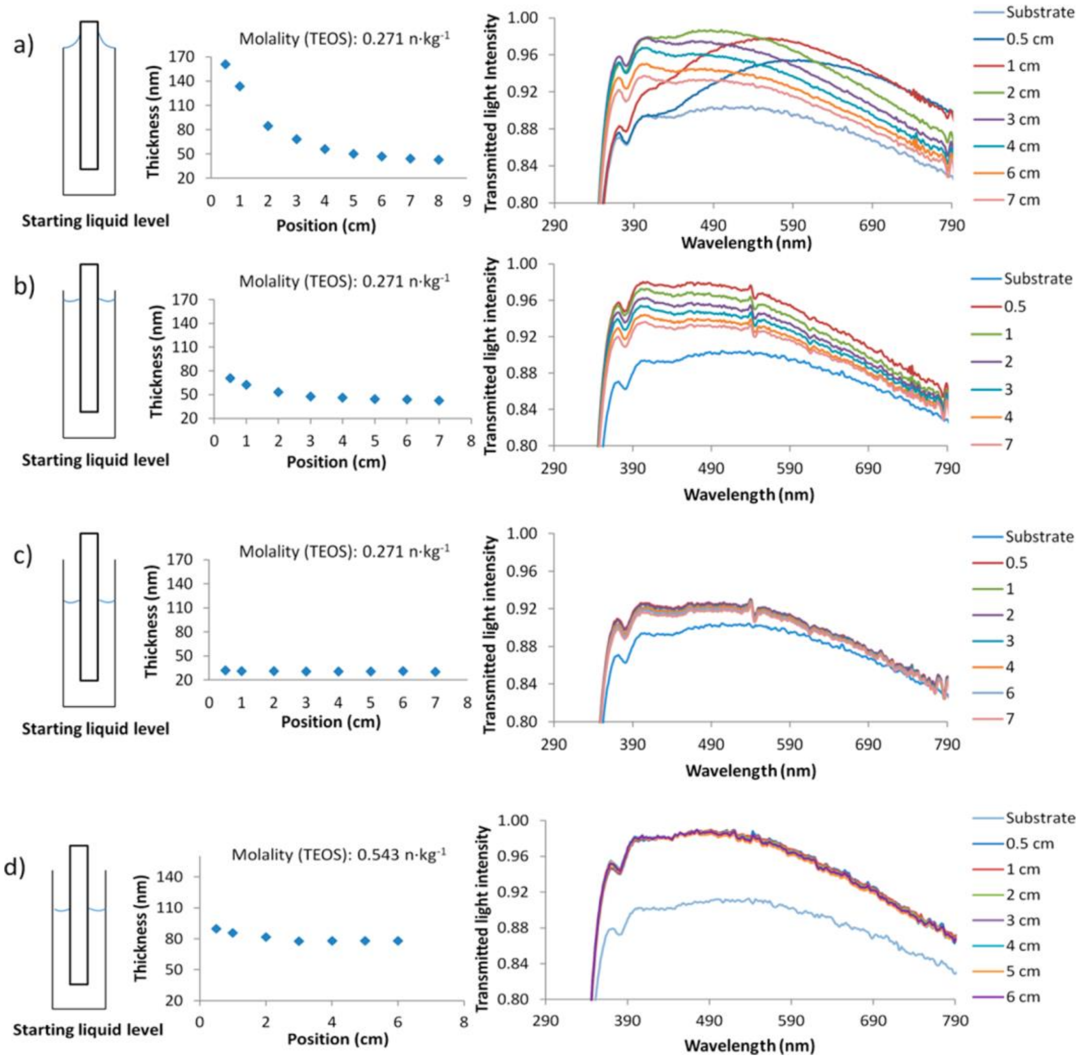
D. Ceratti et al., Adv. Mater. 2015, 27, 4958–4962

Large-surface coatings with a minimum of solution

3) Dip-Coating

The role of the liquid level?

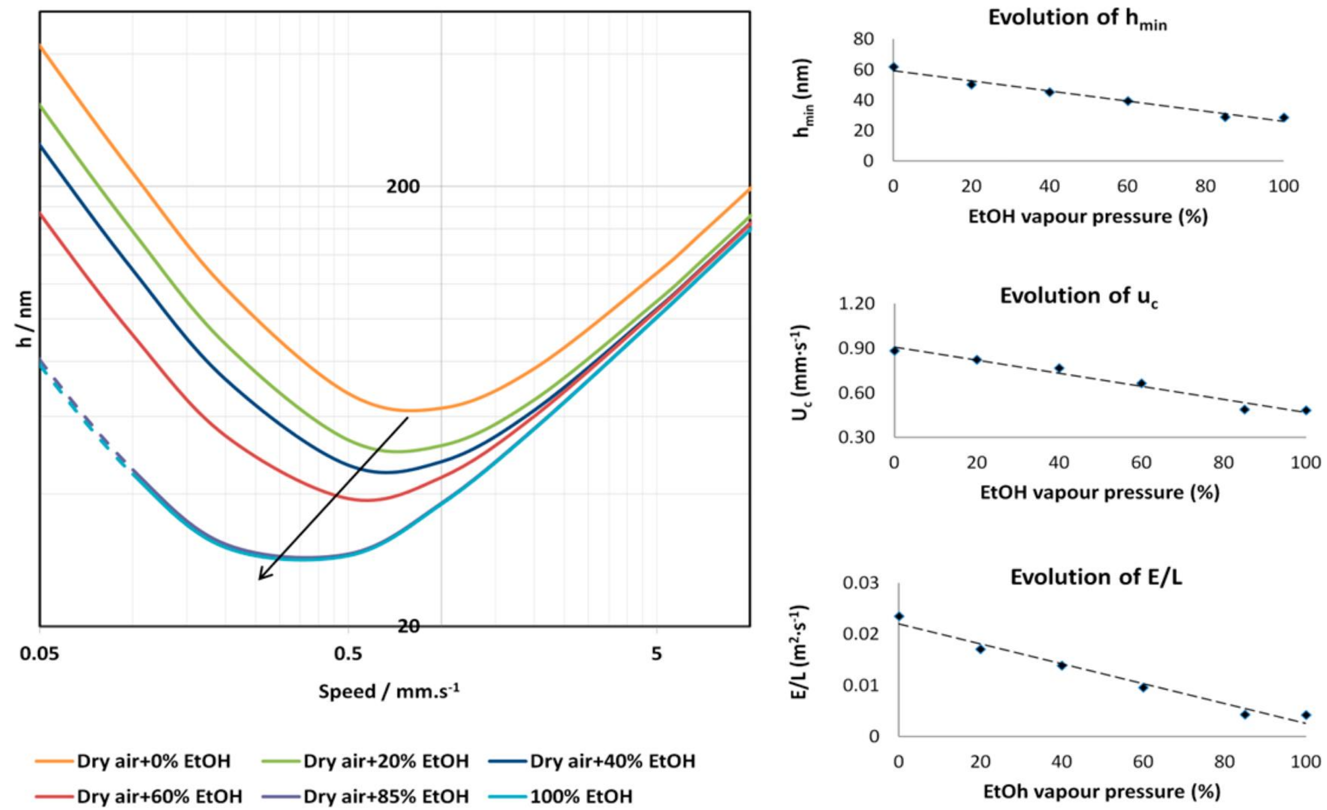
E. Bindini et al., J. Phys. Chem. C 2017, 121, 14572−14580



=> Lowering the liquid level within the container leads to more uniform film deposition, but the layer becomes very thin

3) Dip-Coating

The role of the atmosphere?

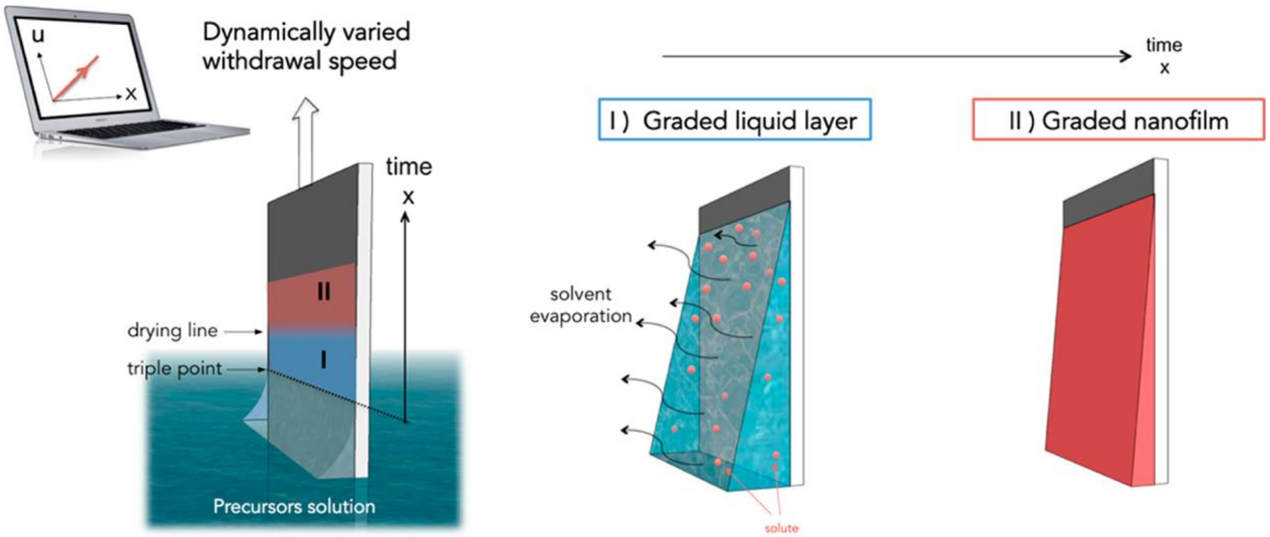


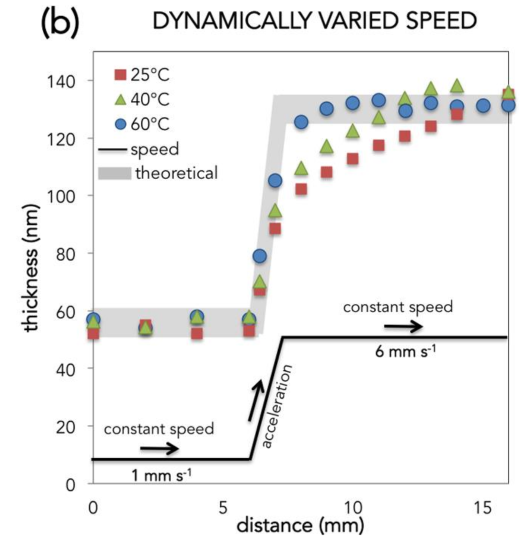
E. Bindini et al., J. Phys. Chem. C 2017, 121, 14572−14580

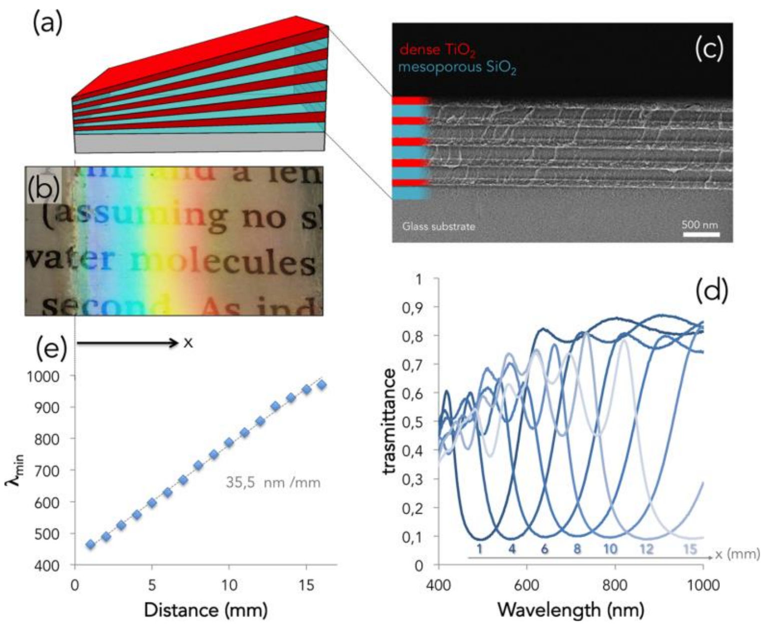
The deposition in the capillary regime can be considerably changed by the atmosphere (increased by using warm air) because it is mainly governed by the evaporation rate.

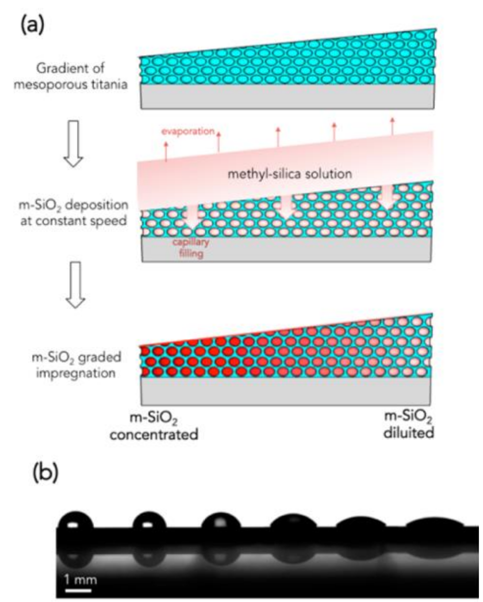
3) Dip-Coating

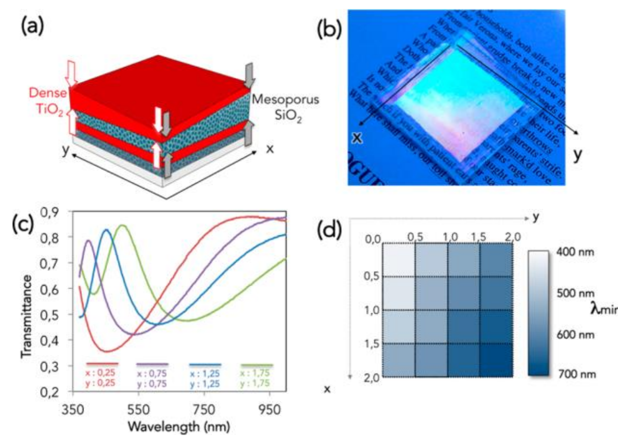
The role of the accelaration?









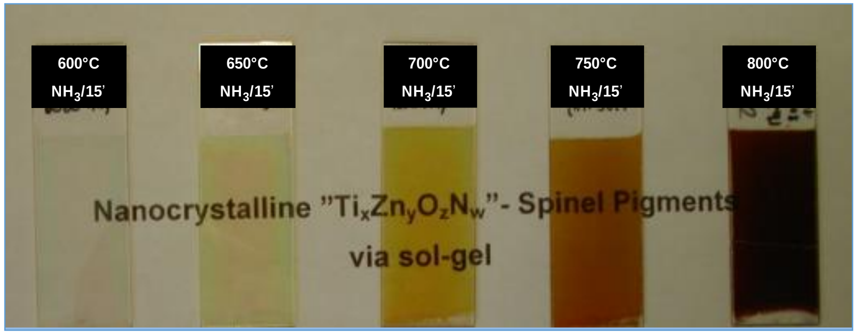


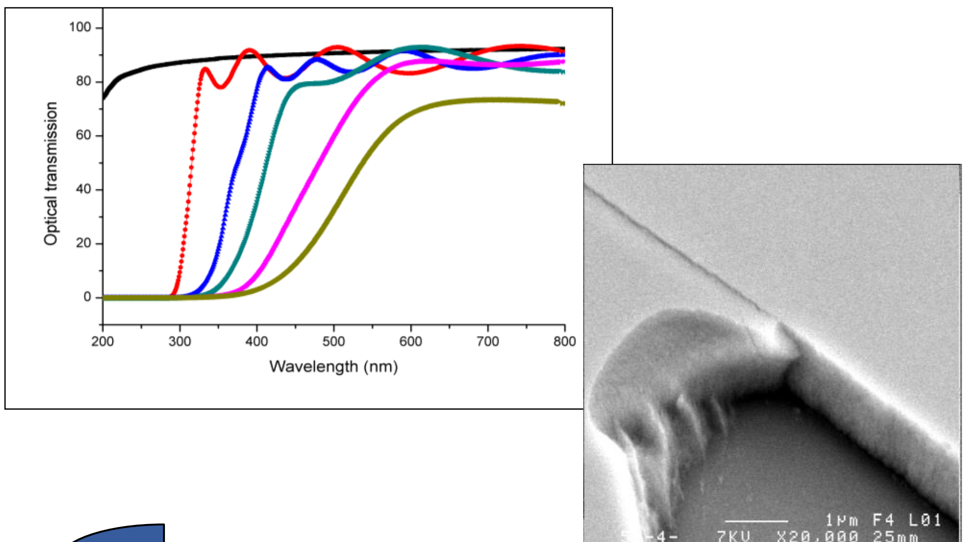
M. Faustini et al., ACS Appl. Mater. Interfaces 2014, 6, 17102−17110

3) Dip-Coating Functional ZnO Nanomaterials

Visible light absorbing transparent thin films

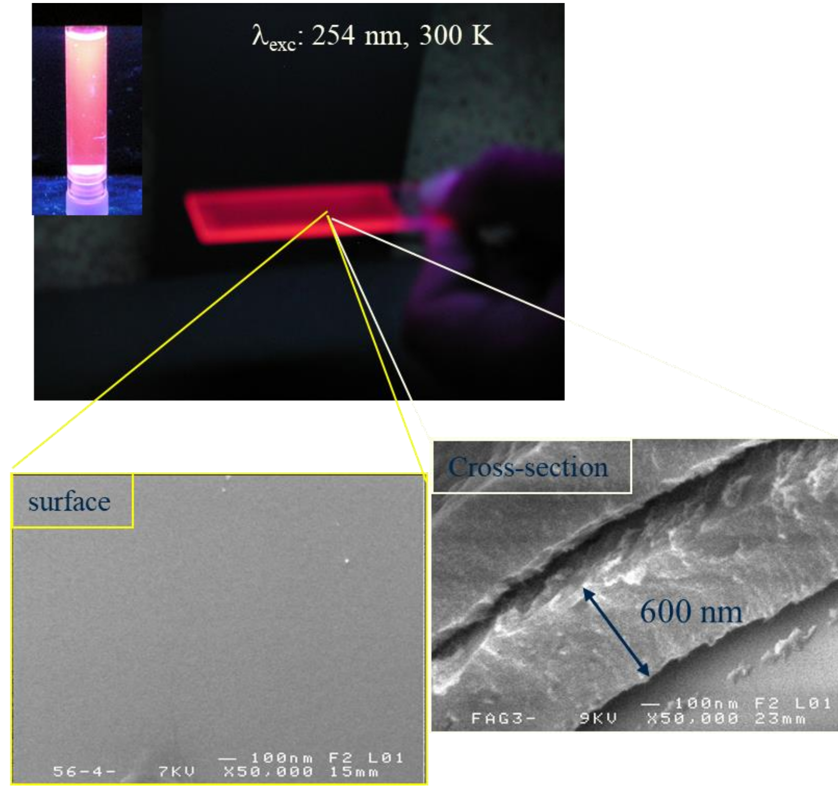
F. Grasset, *et al*., Adv. Mater., *17(3)*, 294, 2005
F. Grasset, *et al*, Superlat. Microstruct., *38*, 300, 2005
D. Berthebaud, *et al*., J. Phys. Chem. C, 111, 7883, 2007
A. Valour, *et al*., Solid State Sci., 54, 30-36, 2016





Optical Band-gap Engineering

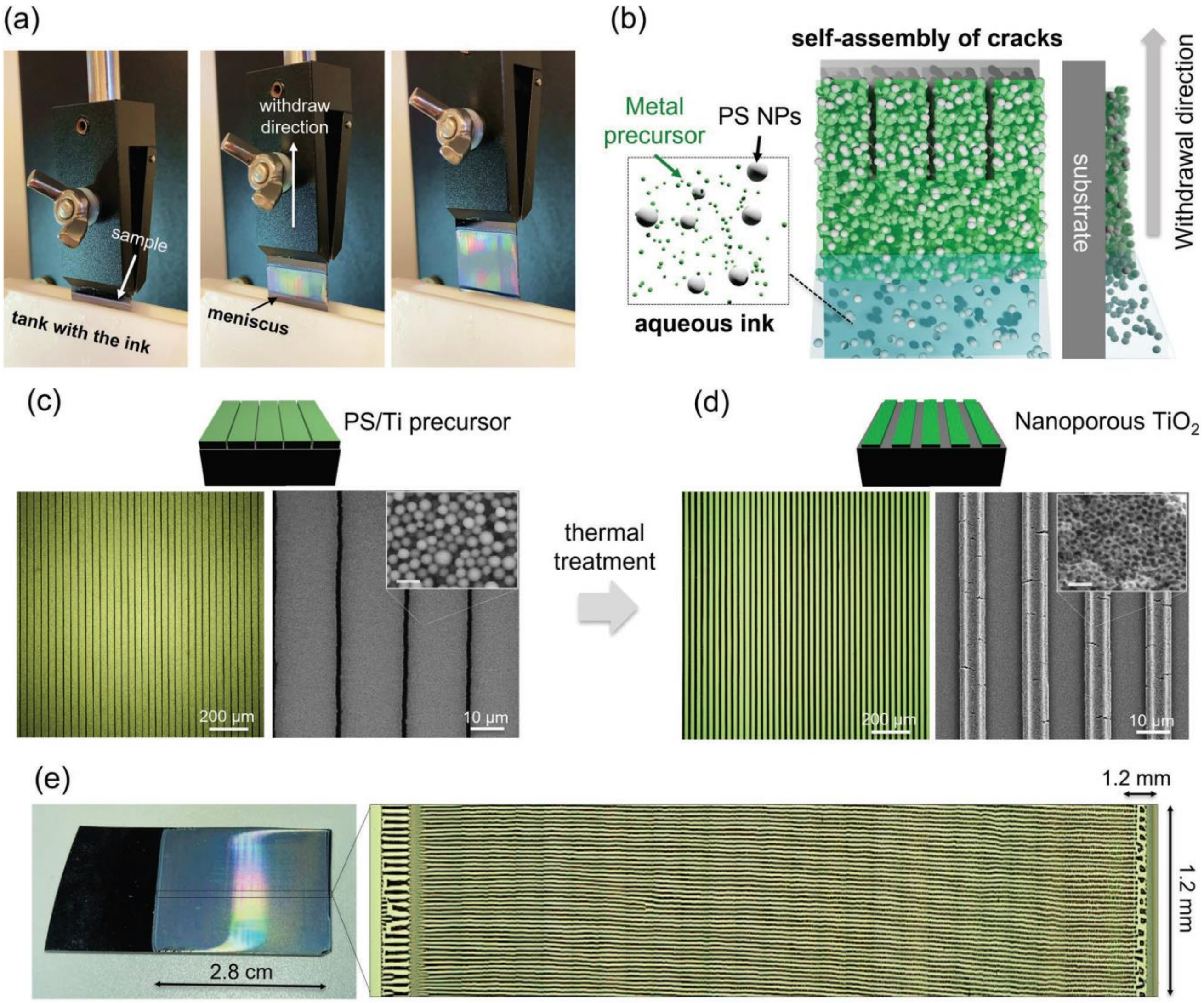
Transparent and Luminescent thin films



T. Aubert, *et al*., Sci. Technol. Adv. Mater., *11*, 044401, 2010

3) Dip-Coating

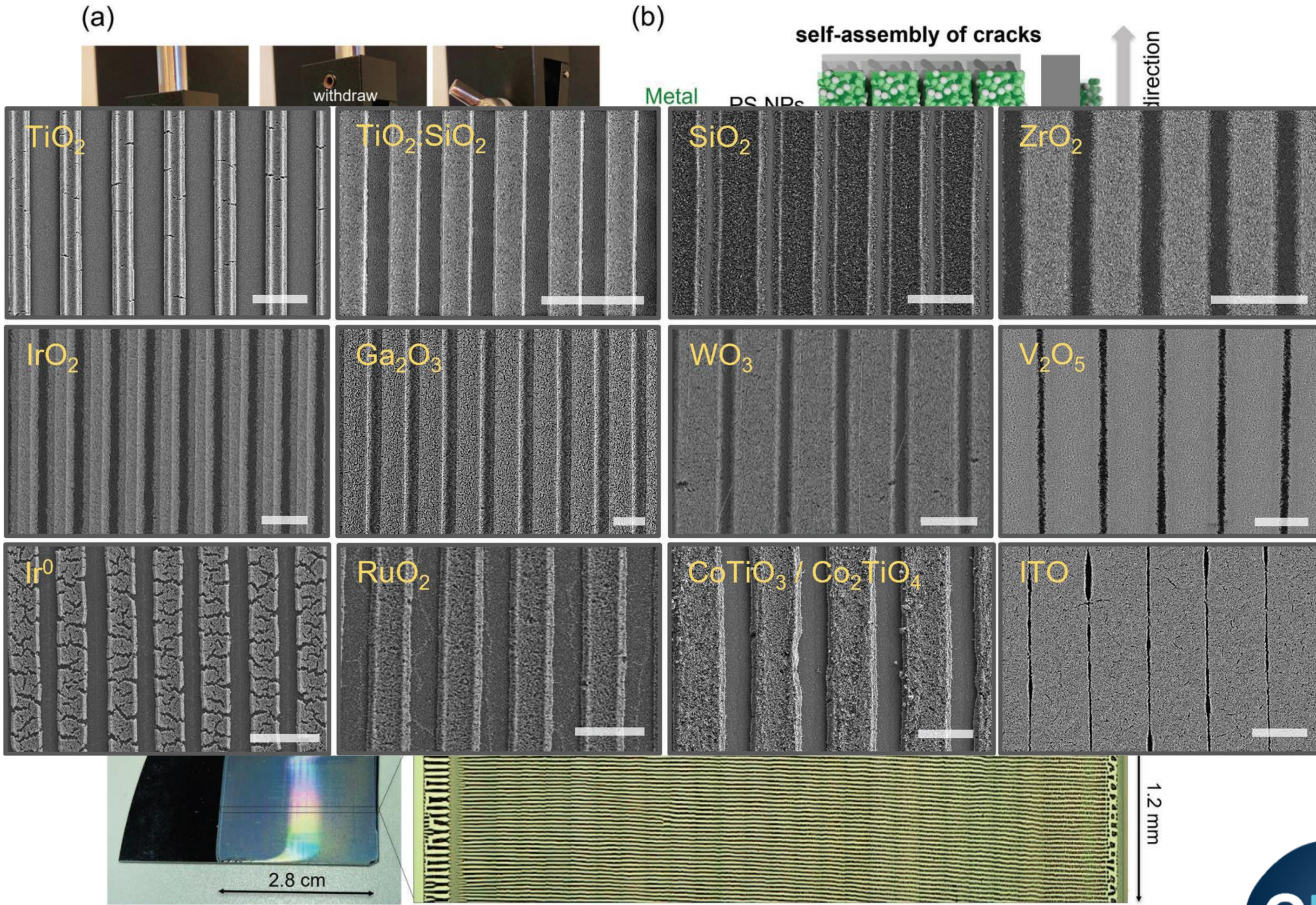
Long-range order of patterned surfaces



M. Odziomek et al., Adv. Mater. **2022**, 34, 2204489

3) Dip-Coating

Long-range order of patterned surfaces



M. Odziomek et al., Adv. Mater. **2022**, 34, 2204489

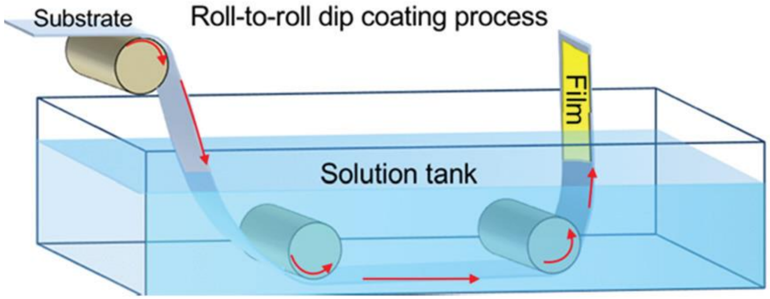
Scale bars represent 30 µm

3) Dip-Coating

Automated dip coating unit

The main advantages:

- Short process,
- Thin and uniform coating,
- Macroscopic and sub-micro length scales,
- Low cost and energy process.



J. Mater. Chem. C, 2020, 8, 9133--9146

The main disadvantages:

- Single substrate batch (?)
- Rigid substrate (?)
- Partially scalable (Stability of the solution)

Outline

1) Introduction

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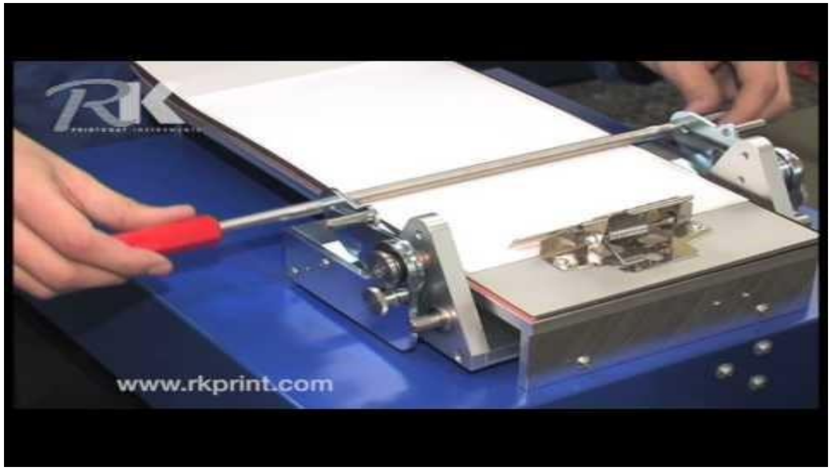
4) Mayer bare coating



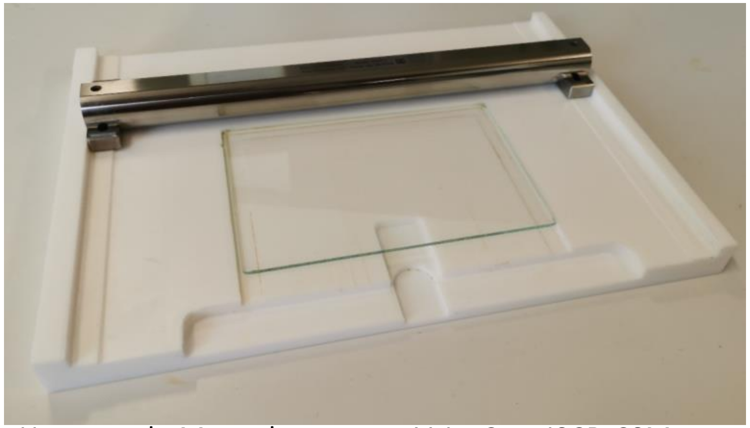
https://youtu.be/dAWQtnUr0Jk

The main advantages:

•Simplicity and very short process,
•Thin and uniform coating,
•Low cost and energy process.

The main disadvantages:

- Single substrate batch
- Thick films (5 to 500 microns)



Homemade Mayer bar coater, V. Le Cam ISCR-CSM

M. Wilmet, Thesis Rennes Univ. 2018
C. Lebastard, Thesis Rennes Univ. 2021

4) Mayer bare coating

agence nationale de la recherche

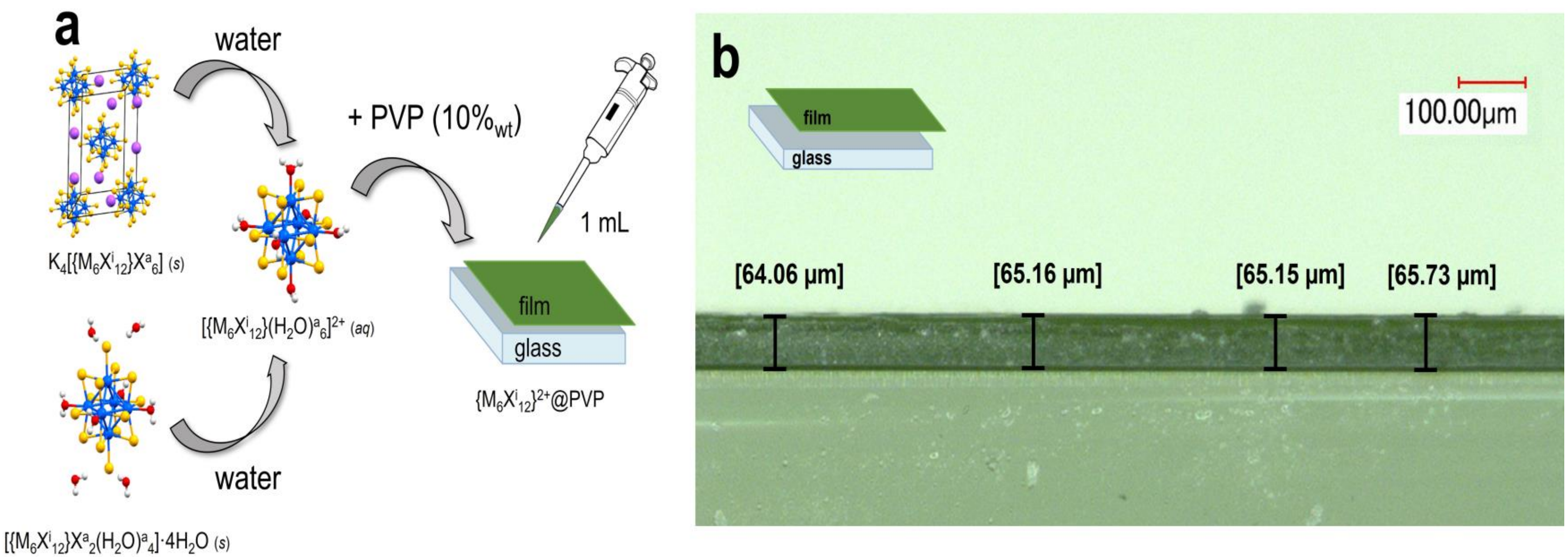
CLuster-based Infrared selectivity MATerials for Energy saving applications

https://anr.fr/Project-ANR-17-CE09-0018

Link IRL 3629

Sciences Chimiques de Rennes UMR CNRS 6226

SAINT-GOBAIN



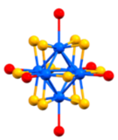
C. Lebastard, *et al.*, Sci. Technol. Adv. Mater., 23(1), 446, 2022

cnrs

4) Mayer bare coating

CLuster-based Infrared selectivity MATerials for Energy saving applications

https://anr.fr/Project-ANR-17-CE09-0018

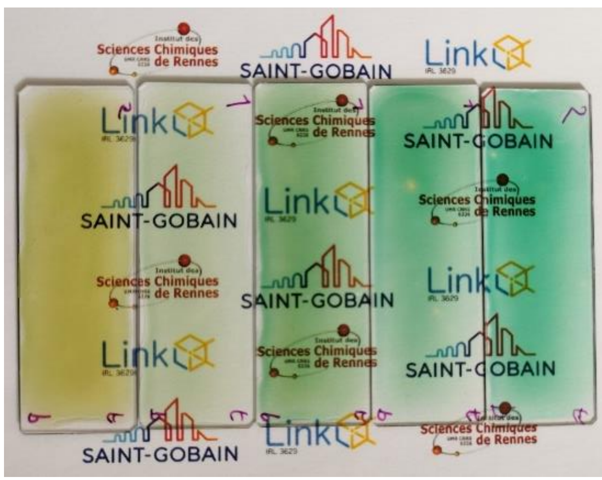


M,M' = Nb, Ta
X = Cl, Br
-4 ≤ n ≤ +2

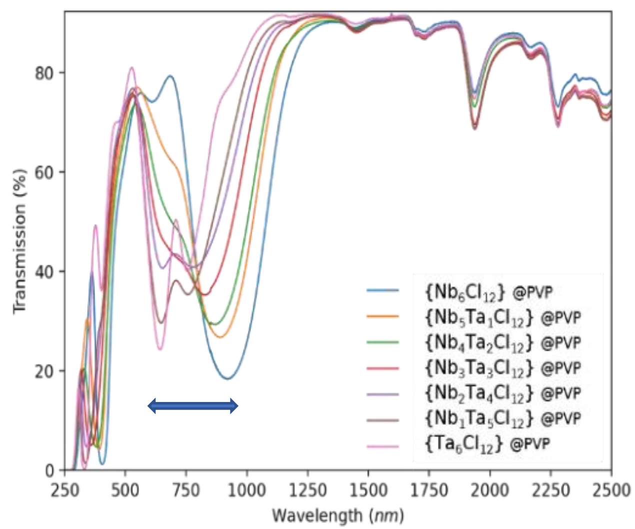
$[(M_{6-x}M'_xX^i_{12})X^a_6]^{n-}$

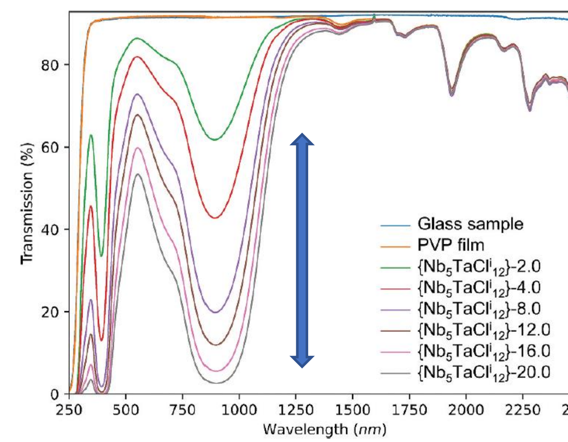
-High transparency

-Tuning of the color and the UV-Vis-NIR absorbance



By Mayer bar coating





M. Wilmet, Thesis Rennes Univ. 2018
C. Lebastard, Thesis Rennes Univ. 2021

C. Lebastard, et al., ACS Appl. Mater. Interfaces, 14, 21116, 2022
C. Lebastard, *et al.*, Nanomaterials, 12, 2052, 2022
C. Lebastard, *et al.*, Sci. Technol. Adv. Mater., 23(1), 446, 2022

4) Mayer bare coating

CLuster-based Infrared selectivity MATerials for Energy saving applications

https://anr.fr/Project-ANR-17-CE09-0018

-High transparency

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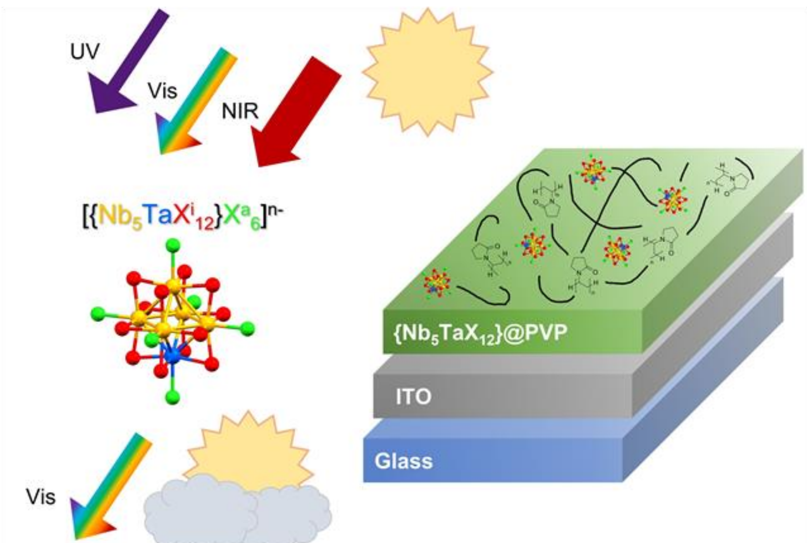

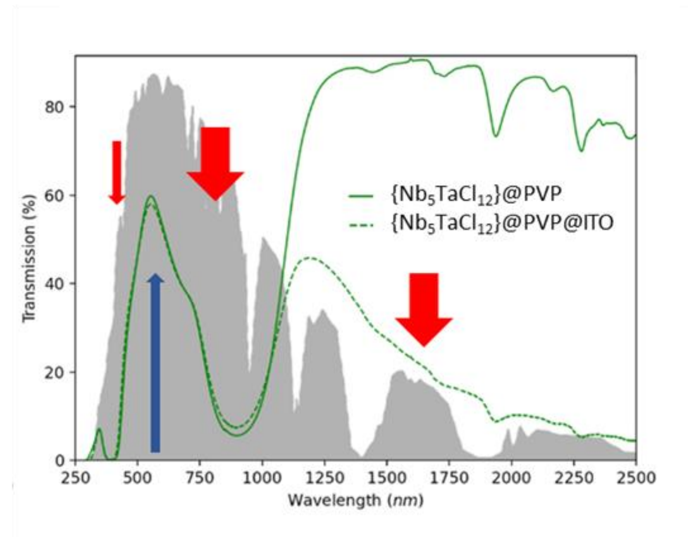

C. Lebastard, *et al.*, Sci. Technol. Adv. Mater., 23(1), 446, 2022

https://theconversation.com/isolation-thermique-et-lumiere-du-soleil-les-defis-des-nouveaux-vitrages-economes-en-energie-204066

Outline

1) Introduction

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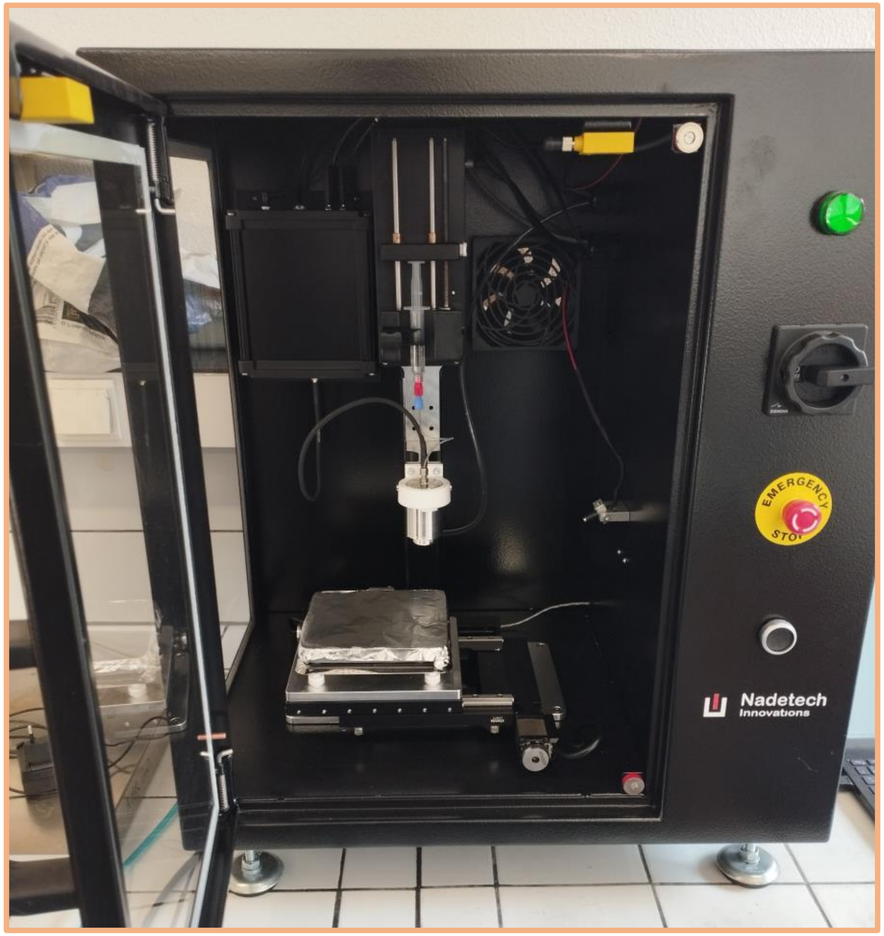
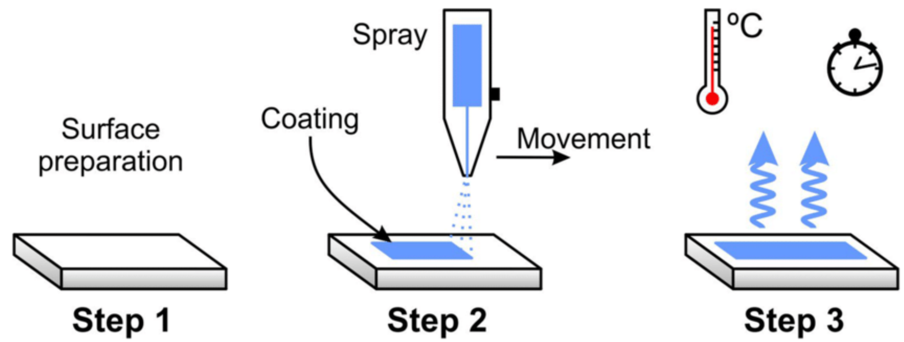
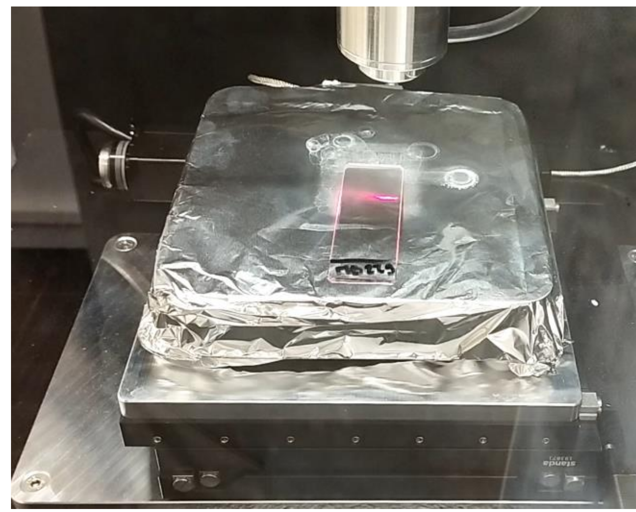
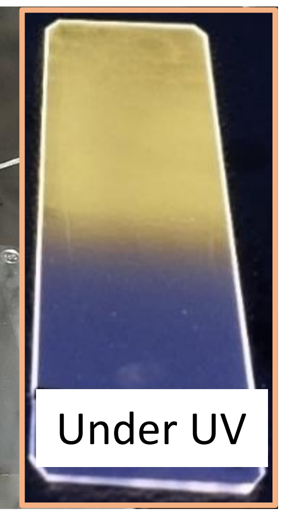
5) Spray-Coating

Spray coating is a technique in which the solution is forced through a nozzle whereby a fine aerosol will be formed







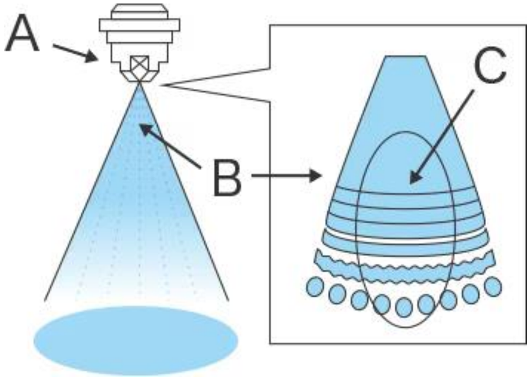


Fabien Grasset

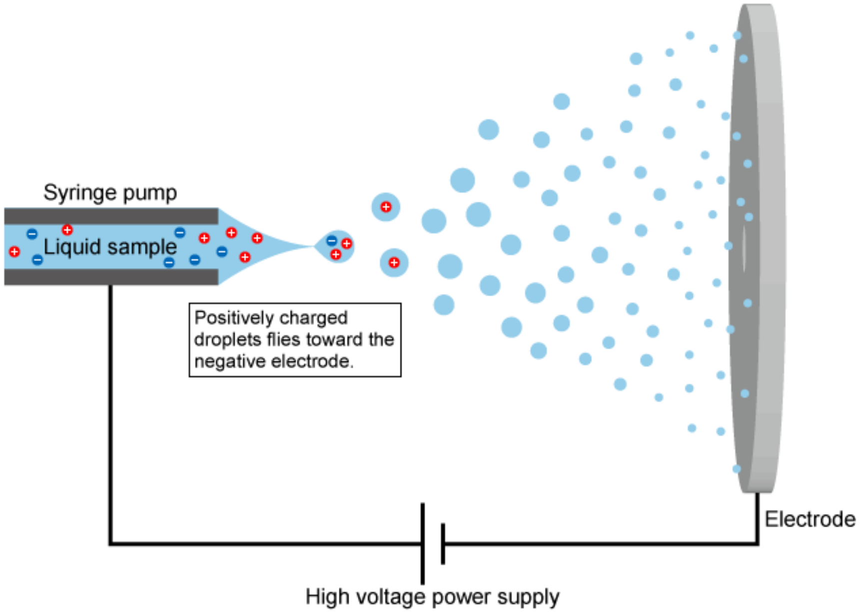
5) Spray-Coating

Spray coaters can be classified into three major groups according to the spray method: Air spray systems, ultrasonic spray systems, and electrostatic spray systems.

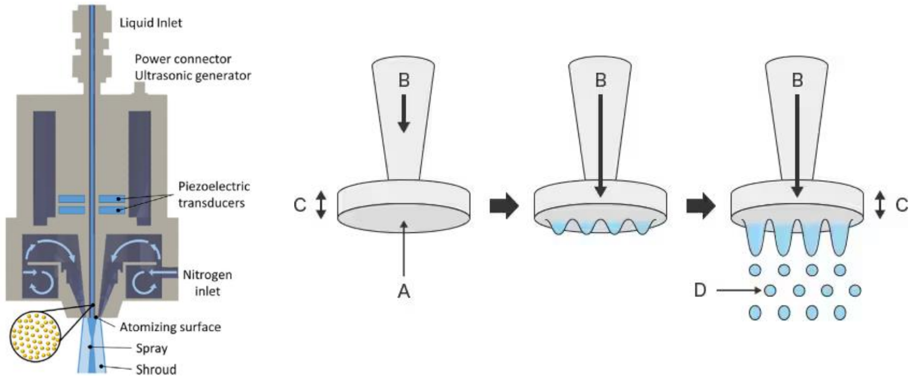
Air spray systems



Electrostatic spray (electrospray) systems

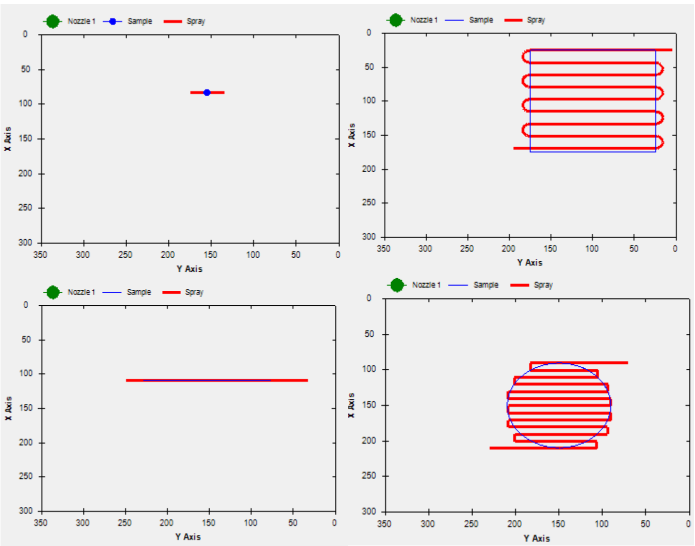


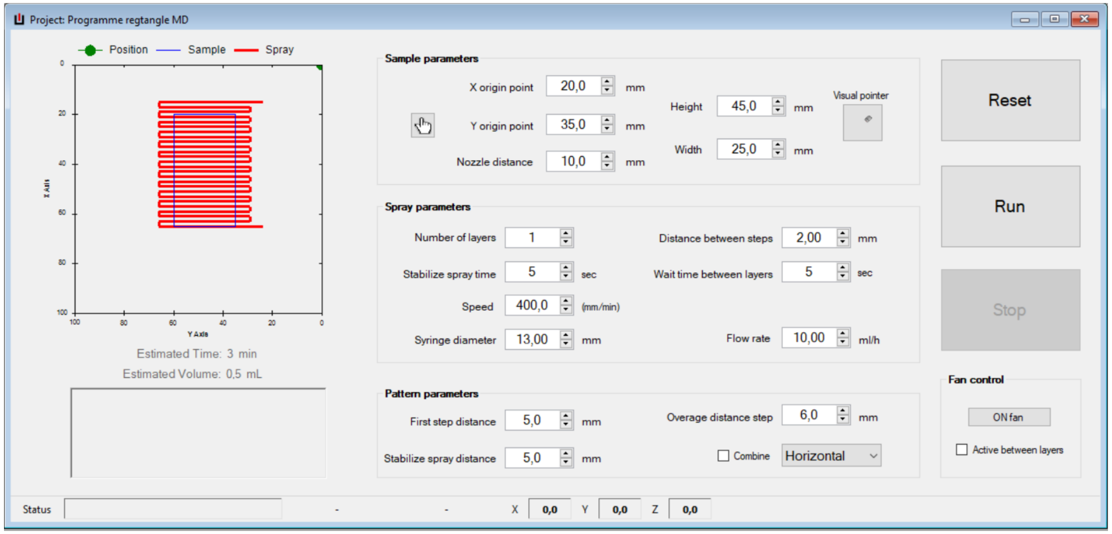
Ultrasonic spray systems



5) Spray-Coating

The distance between the sample and the airbrush, the flow rate, the pressure, the substrate temperature, the concentration of the blend solution, the duration of the spray, the cosolvent mixture, and the number of times the substrate is sprayed are just a few of the process variables for spray coating…





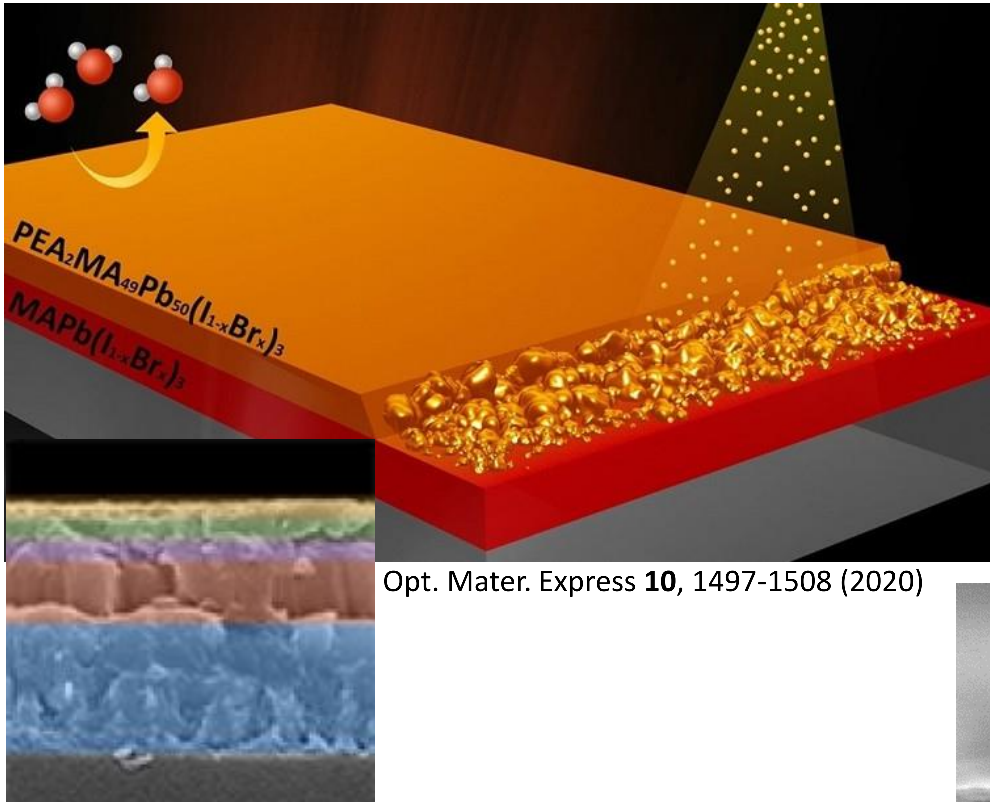
Other important parameters:

-Evaporating temperature of the solvent

-Viscosity of the solvent

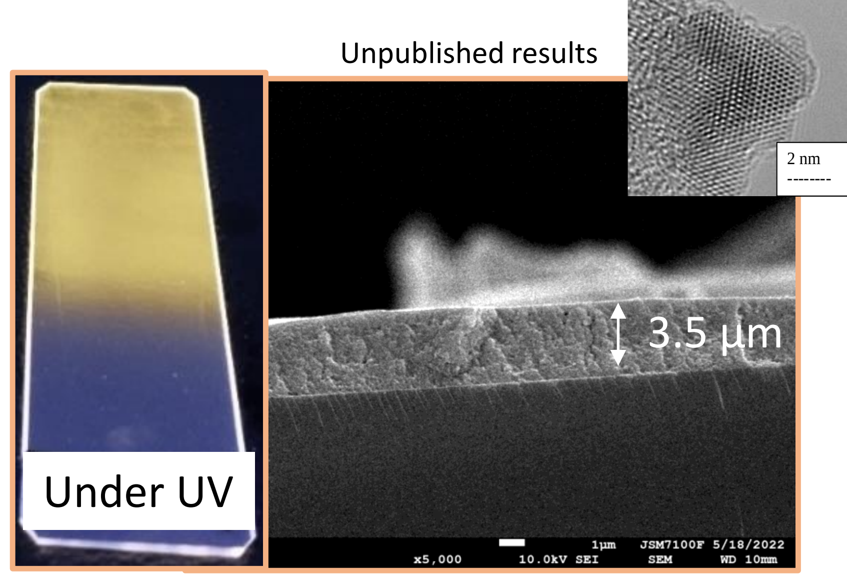
-temperature of the plate

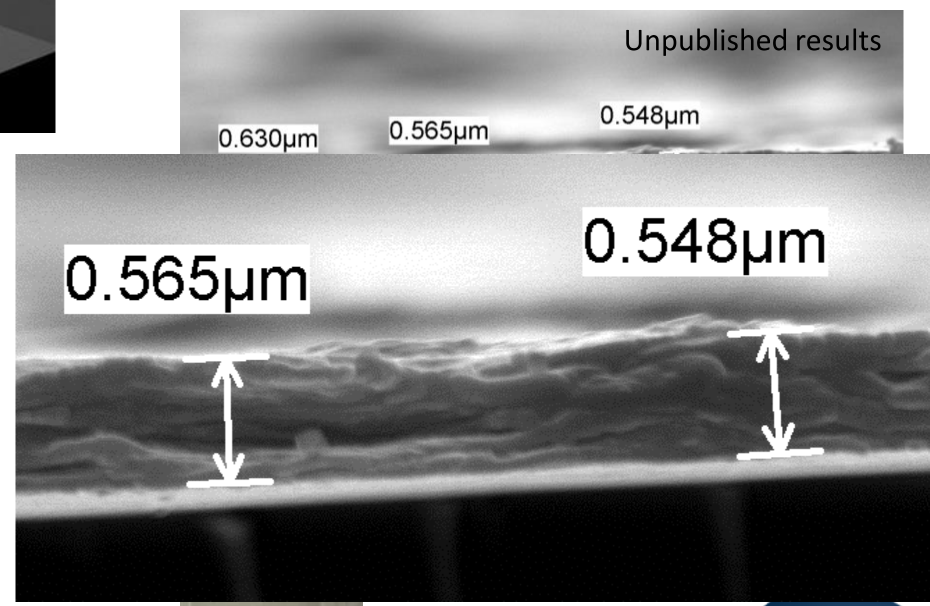
5) Spray-Coating



Opt. Mater. Express **10**, 1497-1508 (2020)

Unpublished results





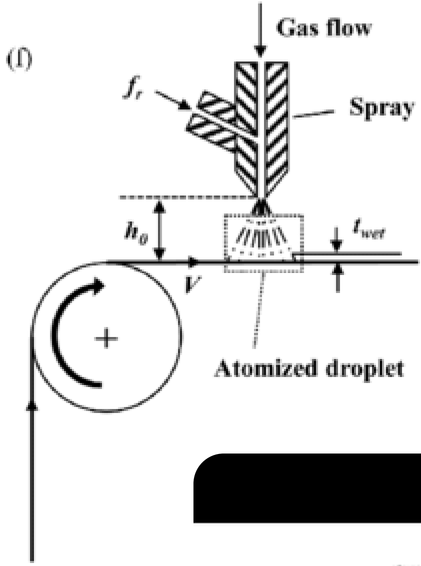
5) Spray-Coating

The main advantages:

•Short process,
•Thick coating,
•Scalable
•Low wasted material

The main disadvantages:

- A lot of parameters
- Thin coating



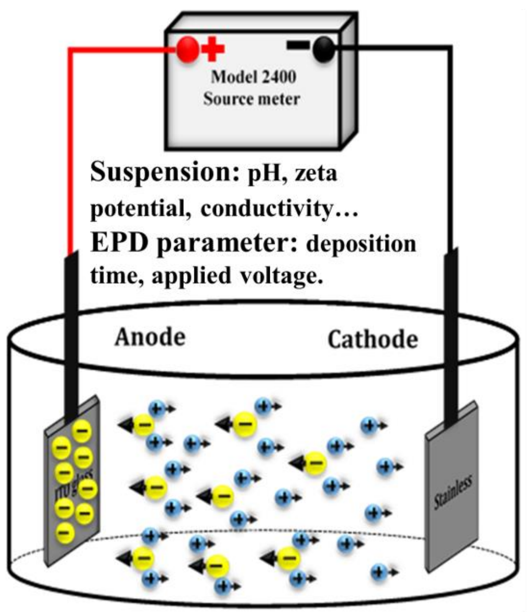
https://youtu.be/R7FnUBrYo1w

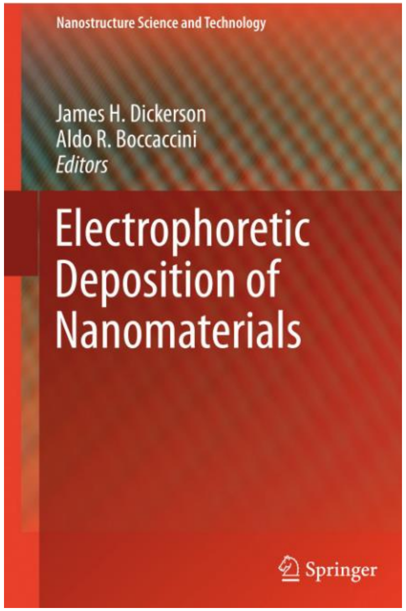
Outline

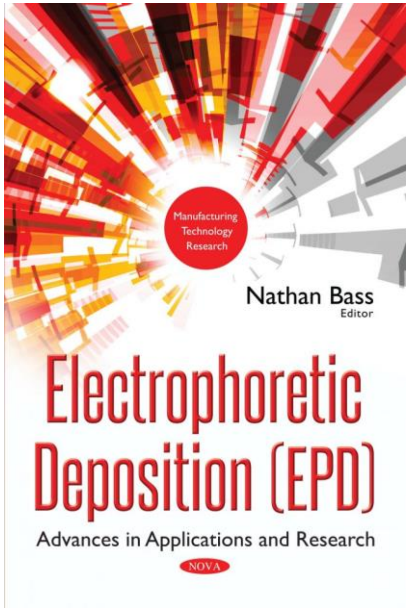
6) EPD

Electrophoretic deposition (EPD) process is based on the **movement** and **deposition** of charged particles under electric field onto a conductive electrode to develop thin or thick films and coatings. The EPD process has been known for more than two centuries

EPD can be applied for a wide range of fine powder or colloidal particles of metals, ceramics, polymers, and the composites.

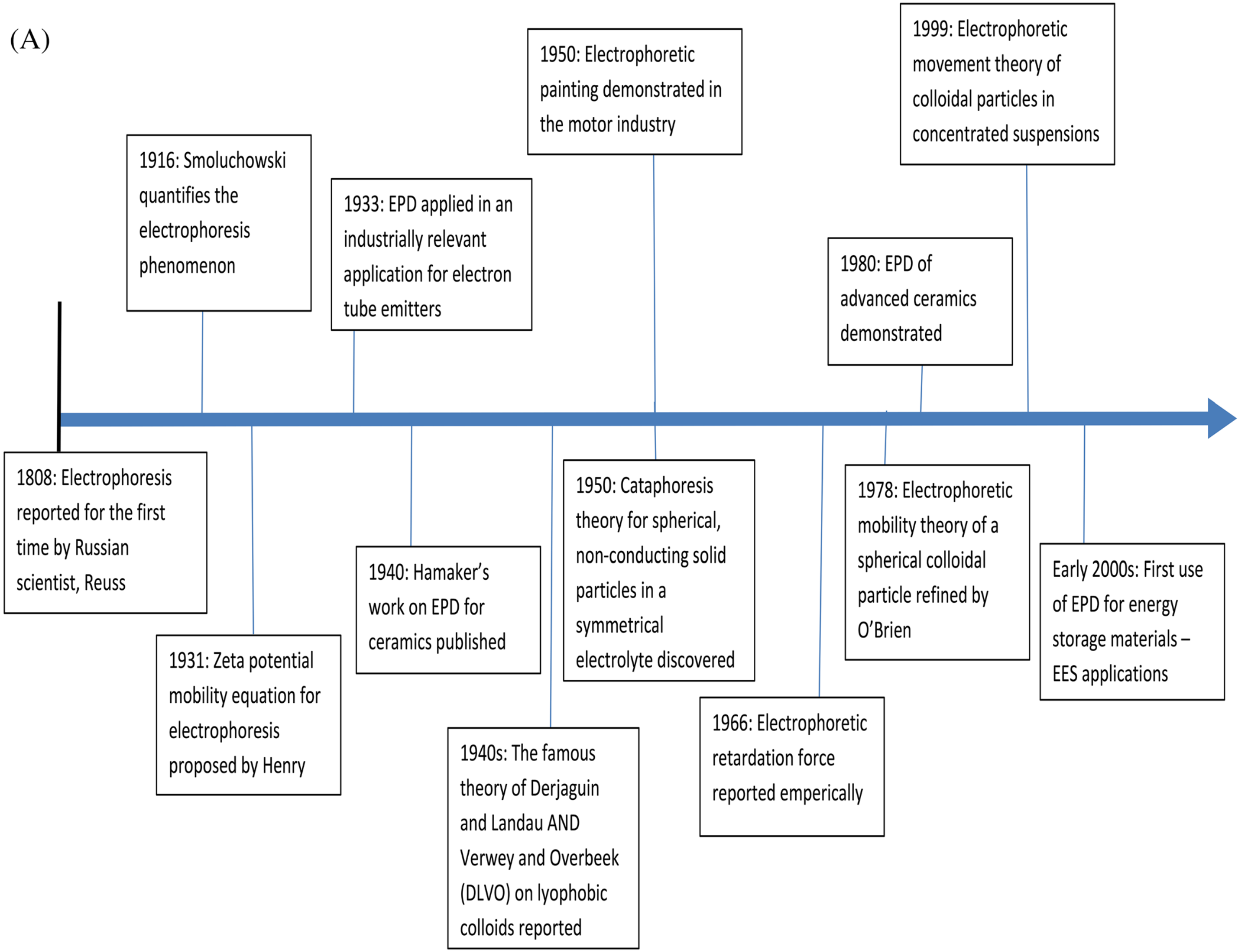






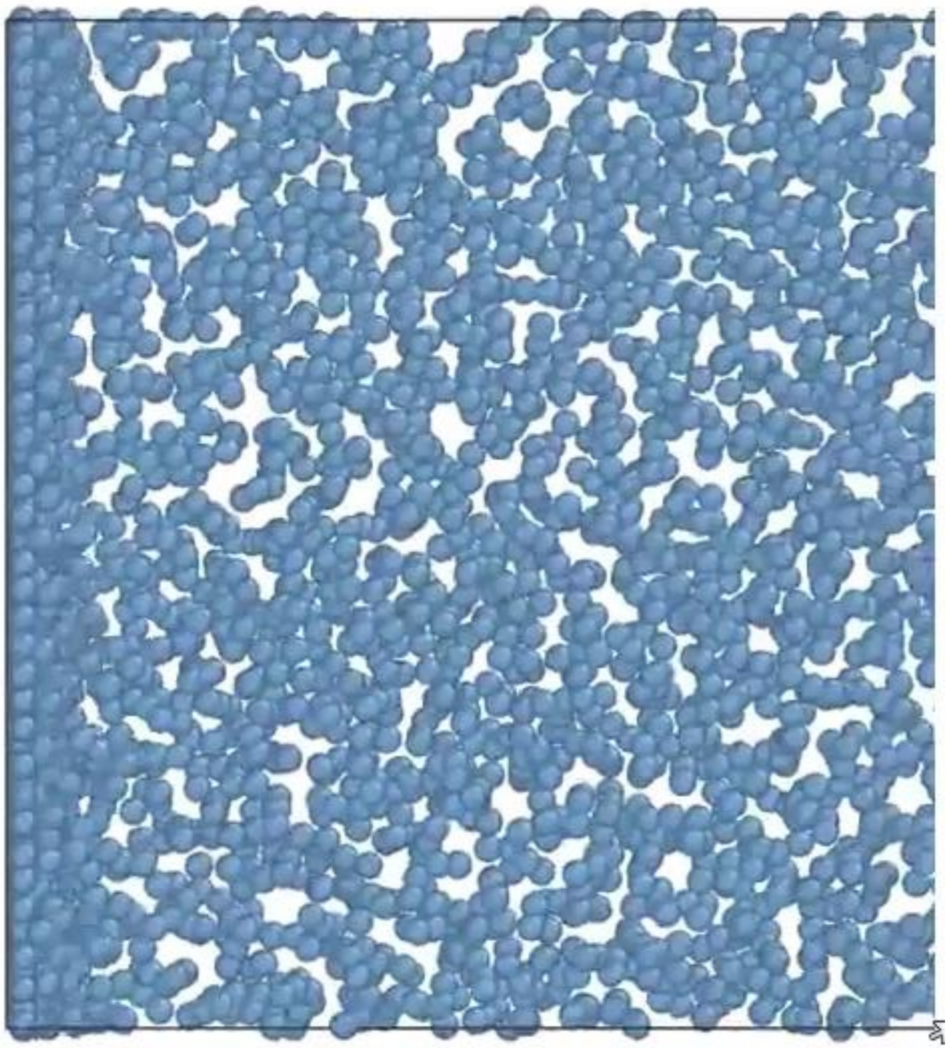
6) EPD

(A)

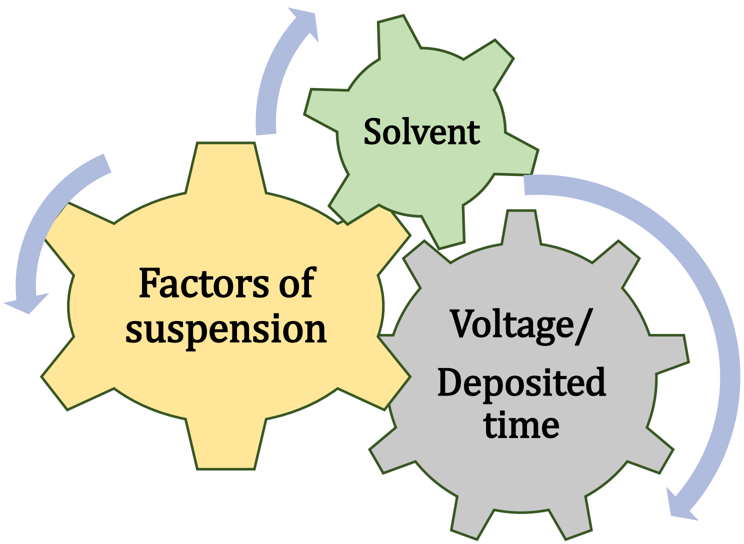

1808: Electrophoresis reported for the first time by Russian scientist, Reuss
1916: Smoluchowski quantifies the electrophoresis phenomenon
1931: Zeta potential mobility equation for electrophoresis proposed by Henry
1933: EPD applied in an industrially relevant application for electron tube emitters
1940: Hamaker's work on EPD for ceramics published
1940s: The famous theory of Derjaguin and Landau AND Verwey and Overbeek (DLVO) on lyophobic colloids reported
1950: Electrophoretic painting demonstrated in the motor industry
1950: Cataphoresis theory for spherical, non-conducting solid particles in a symmetrical electrolyte discovered
1966: Electrophoretic retardation force reported emperically
1978: Electrophoretic mobility theory of a spherical colloidal particle refined by O'Brien
1980: EPD of advanced ceramics demonstrated
1999: Electrophoretic movement theory of colloidal particles in concentrated suspensions
Early 2000s: First use of EPD for energy storage materials – EES applications

6) EPD

Courtesy of LLNL (USA)



Deposition is generally described by a two-step process. It occurs when electric-field driven colloidal particles suspended in a fluid migrate toward an electrode (step 1) where they assemble or coagulate into a deposit (step 2).



A lot of factors influencing EPD, and most of them are inter-related.

Sciences Chimiques de Rennes UMR CNRS 6226

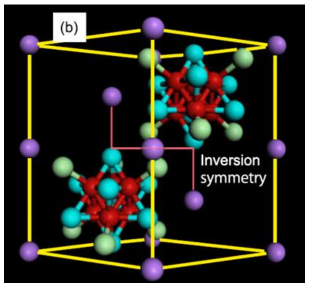
P.I.: S. Cordier

Transition Metal Atom Clusters

From solid state synthesis to colloidal solution

Gas-solid reaction: K. Kirakci, *et al.* Z. Anorg. Allg. Chem. *631*, 411416, 2005

$$18\ Br_{2(g)} + 12\ Mo_{(s)} \xrightarrow[N2]{680^\circ C} 12\ MoBr_3 \xrightarrow{680^\circ C} 6MoBr_2 + 2\ CsBr \xrightarrow[\text{Vacuum/3 days}]{950^\circ C} Cs_2Mo_6Br_{14}$$



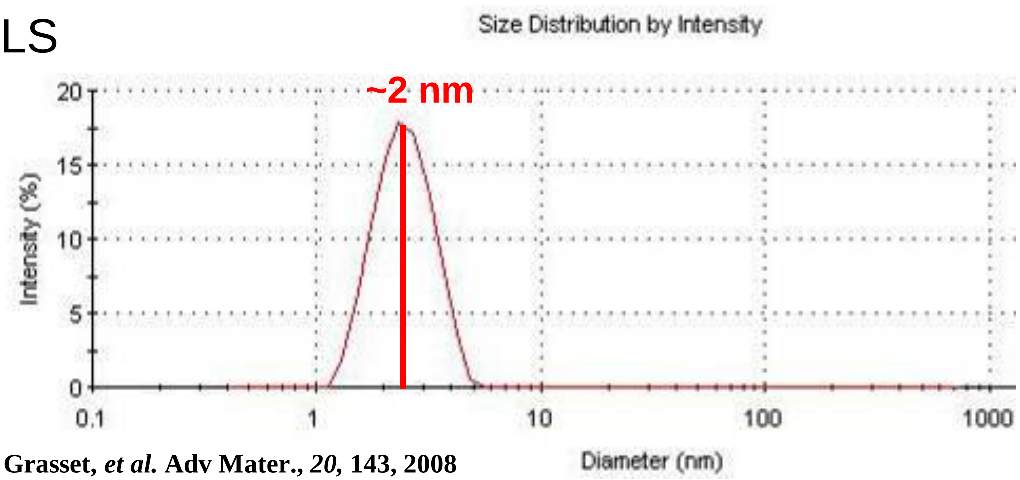
N. Saito, *et al.* Inorg. Chem. *56*, 6234, 2017

Solvent media

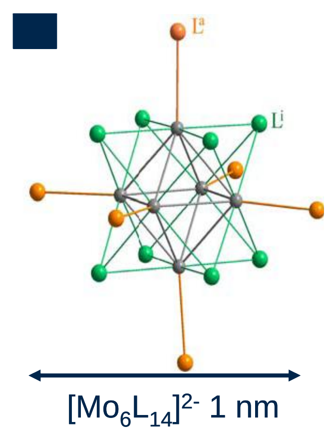
$Cs_2Mo_6Br_{14}$ ⟺ $2Cs^+ + [Mo_6Br_{14}]^{2-}$

Molecular character

DLS



F. Grasset, *et al.* Adv Mater., *20*, 143, 2008



"True nanoobject"

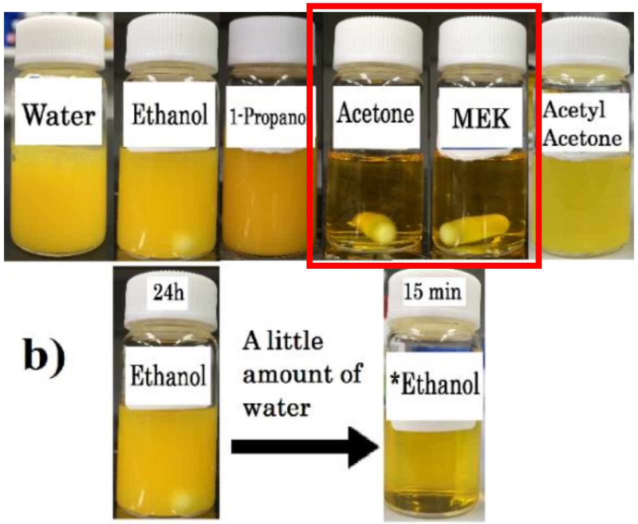
Difficult to prepare thin film by CSD

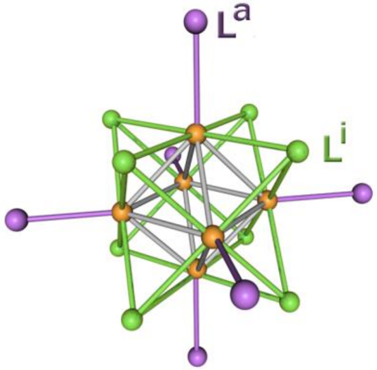
Fabien Grasset

13th June 2023, EI NANO

6) EPD

Electrophoretic Deposition of $[Mo_6Br_{14}]^{2-}$



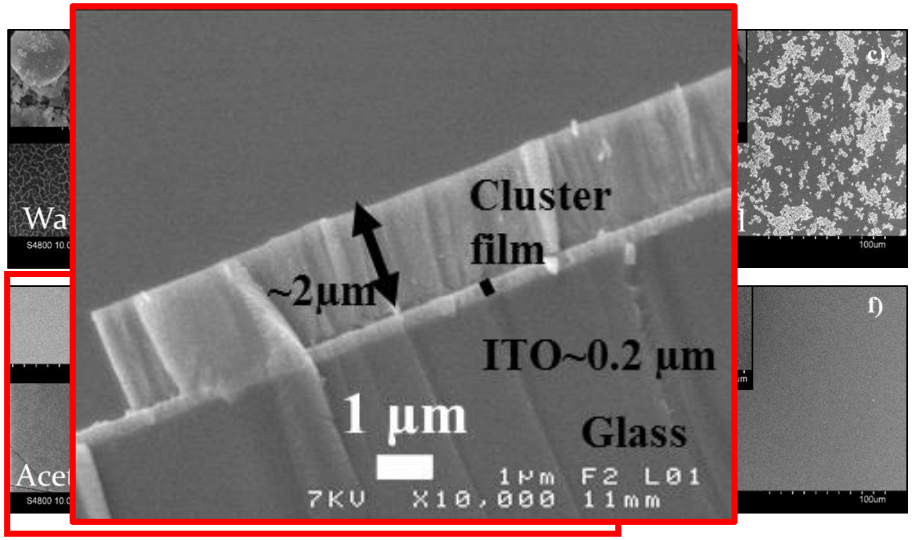


Best deposition parameters:

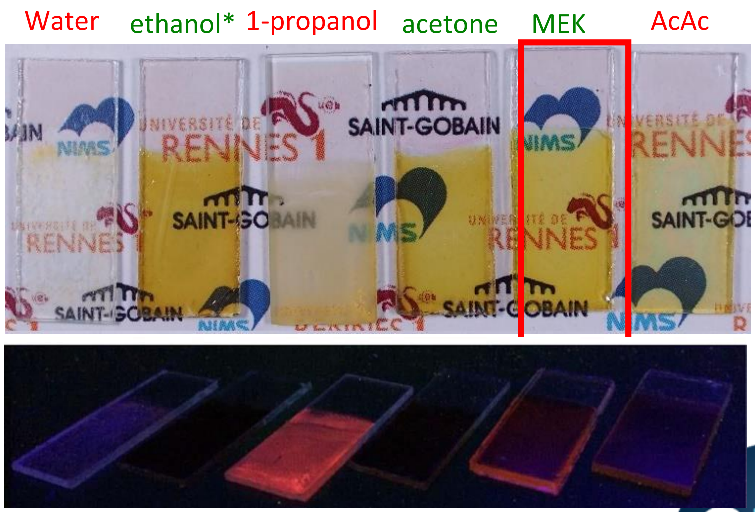
-*Methyl ethyl ketone* (butanone)
-*Acetone*

-15V~20V and 40 s

=> Film thickness from 0.5 to 2 µm in less than 10-40 s



N.T.K. Nguyen *et al.*, ECS J. Solid State Sci. Technol., 2016, 5 (10) R178-R186



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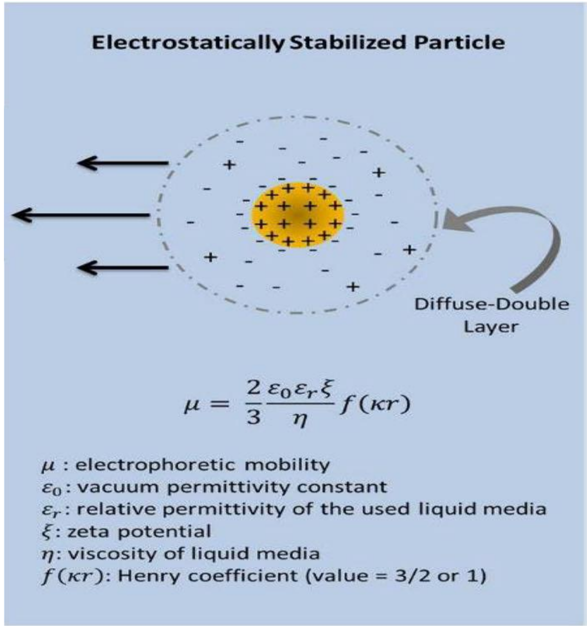
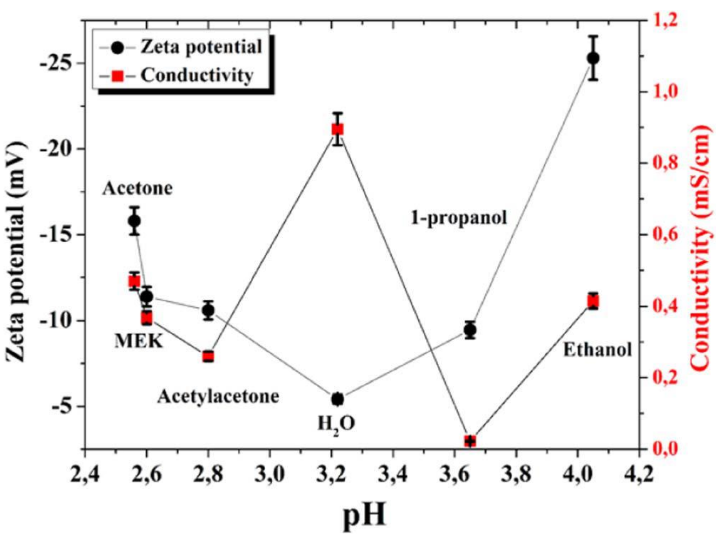
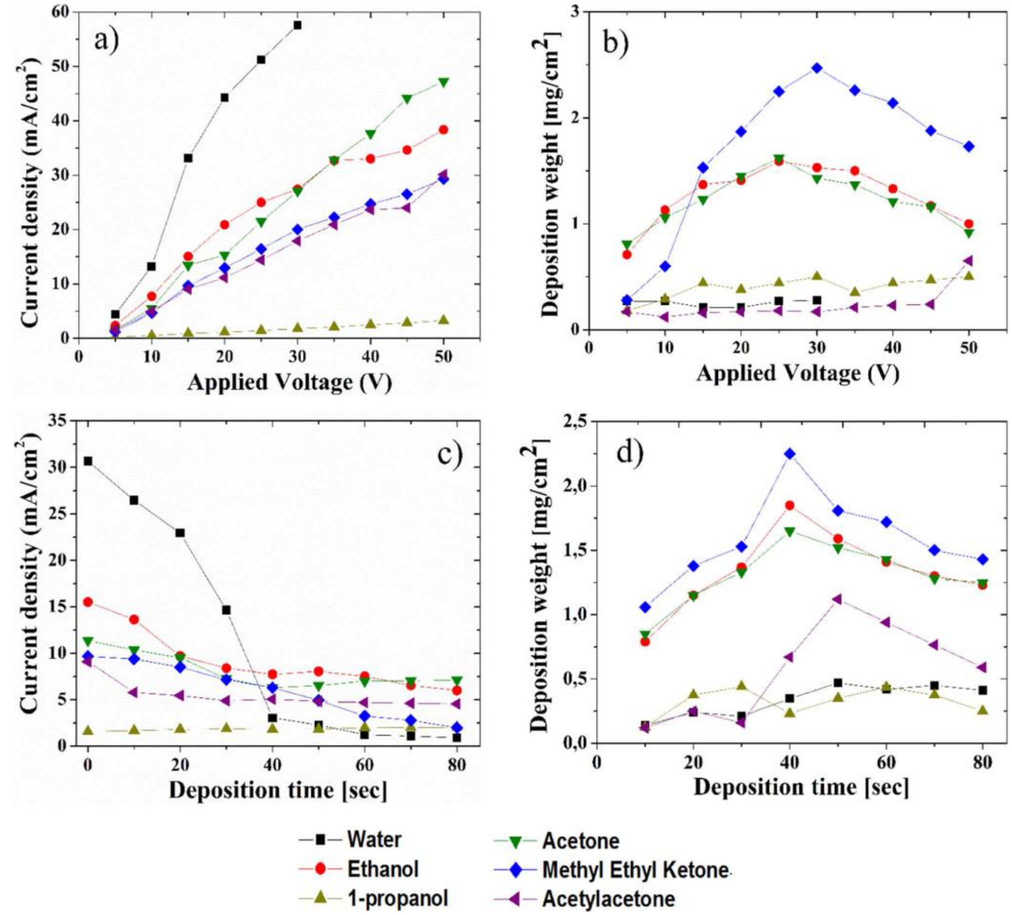
6) EPD



B.K. Chakrabarti et al., Int J Energy Res. 2022;46:13205–13250.



Current density and Deposition weight:
-Applied voltage
-Deposition time

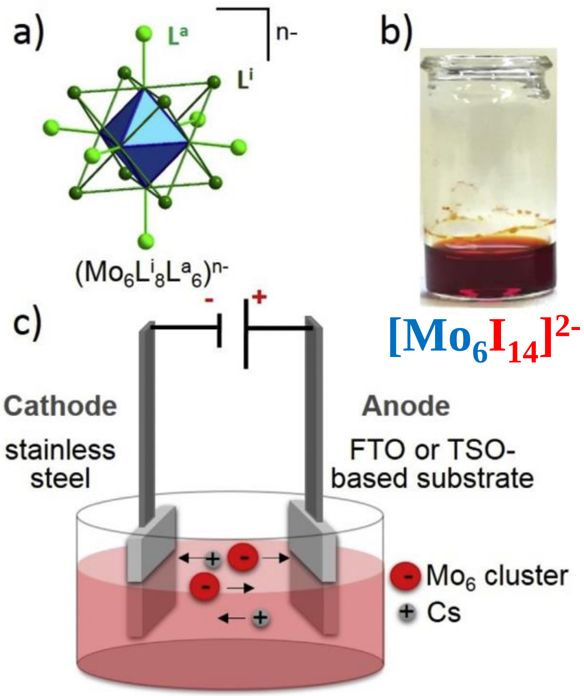


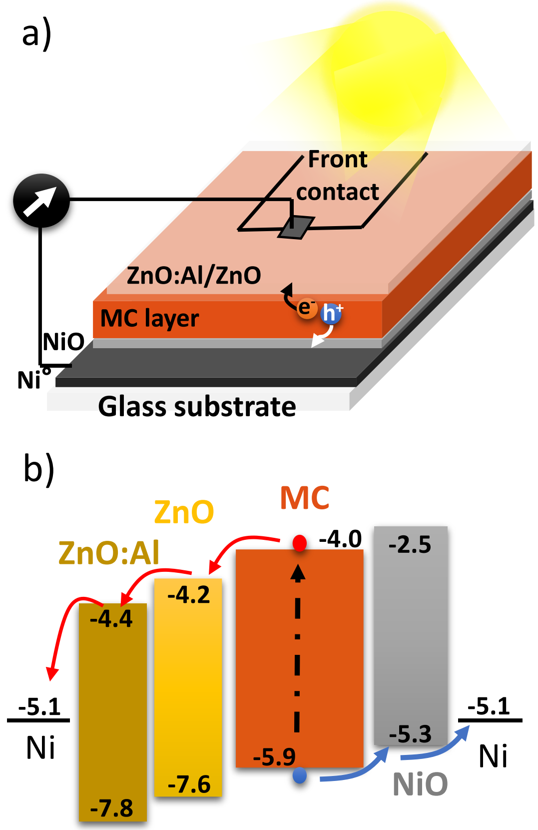
N.T.K. Nguyen *et al.*, ECS J. Solid State Sci. Technol., 2016, 5 (10) R178-R186

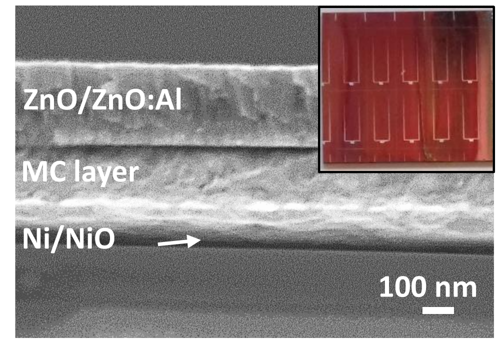
A. Renaud

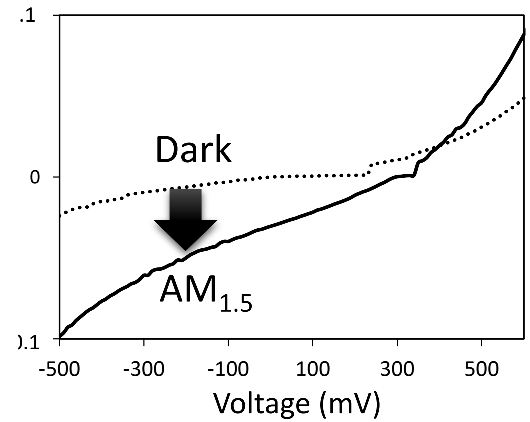
Transparent Thin Films for PV Application

Evidences of the Ambipolar Behaviour of Mo6 cluster iodides in All Inorganic Solar Cells

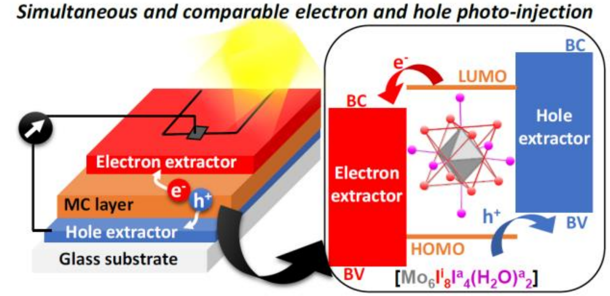








Simultaneous and comparable electron and hole photo-injection



A. Renaud, *et al.*, ACS Appl. Mater. Interfaces, 2022, 14, 1347

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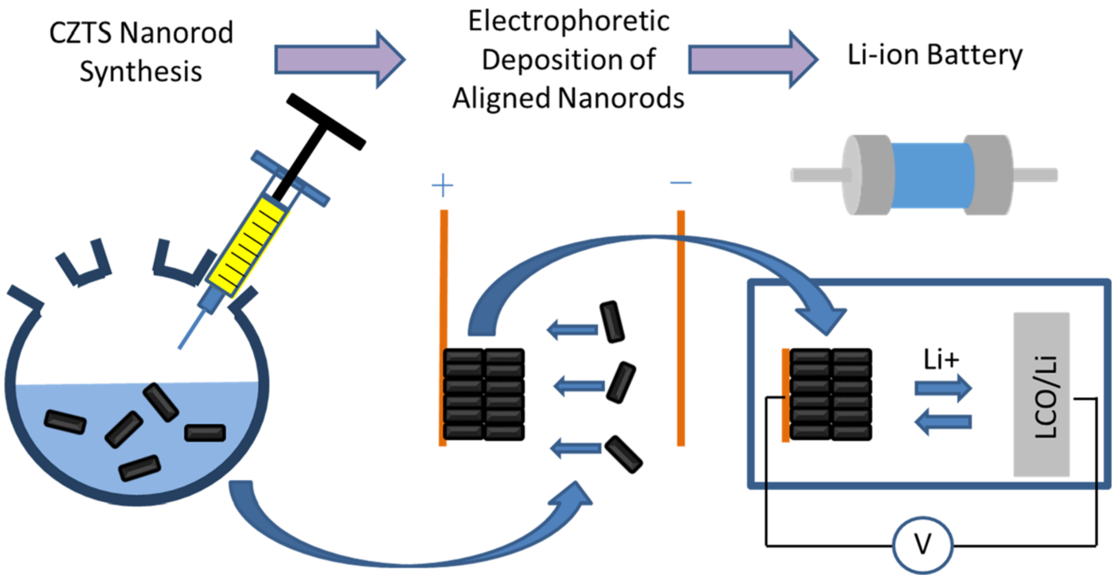
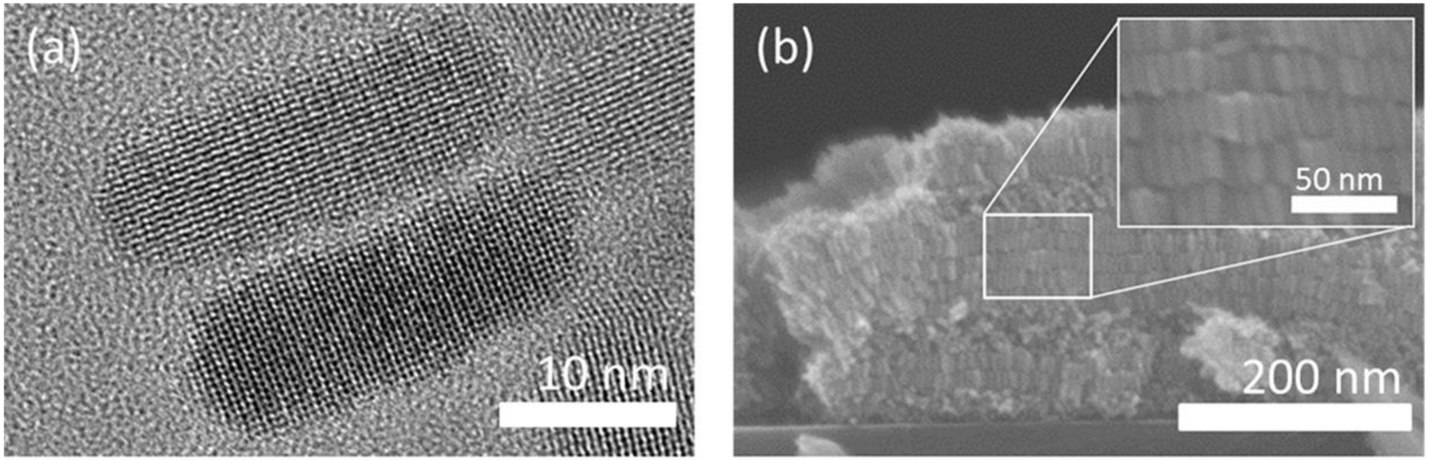
6) EPD



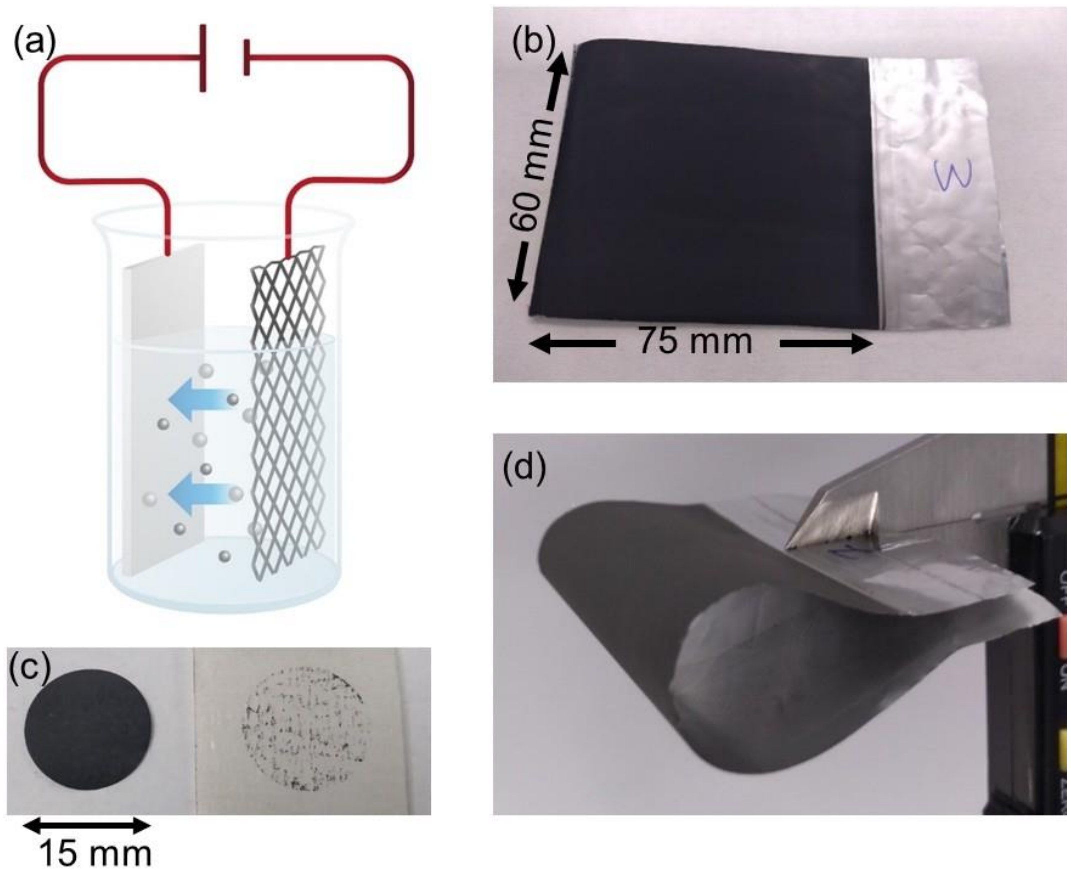
Aligned Copper Zinc Tin Sulfide Nanorods as Lithium-Ion Battery Anodes with High Specific Capacities



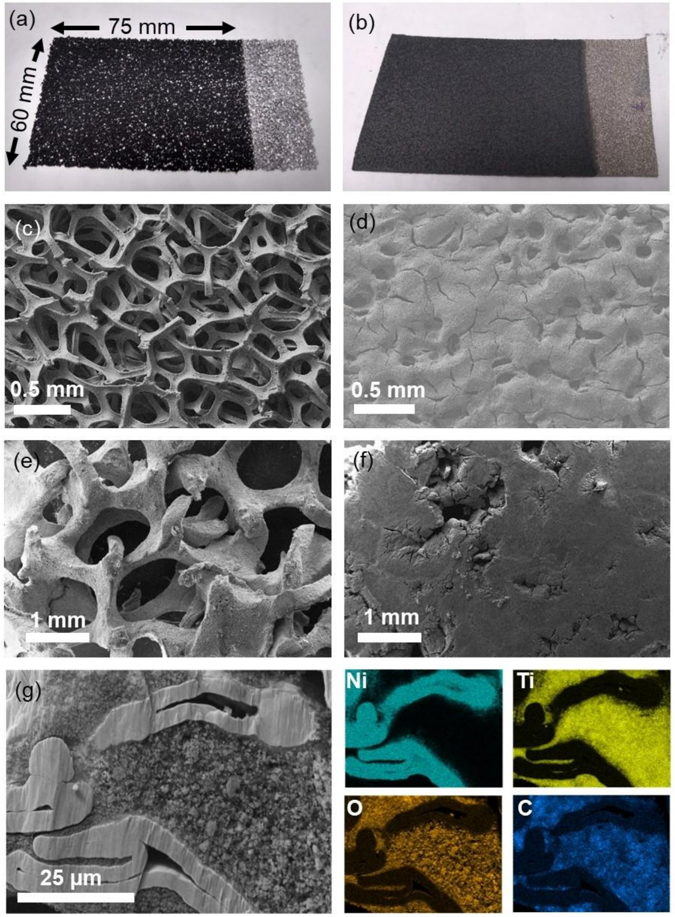
G. Bree et al., J. Phys. Chem. C 2018, 122, 20090−20098

6) EPD

Full Cell Lithium-Ion Battery Manufacture by Electrophoretic Deposition



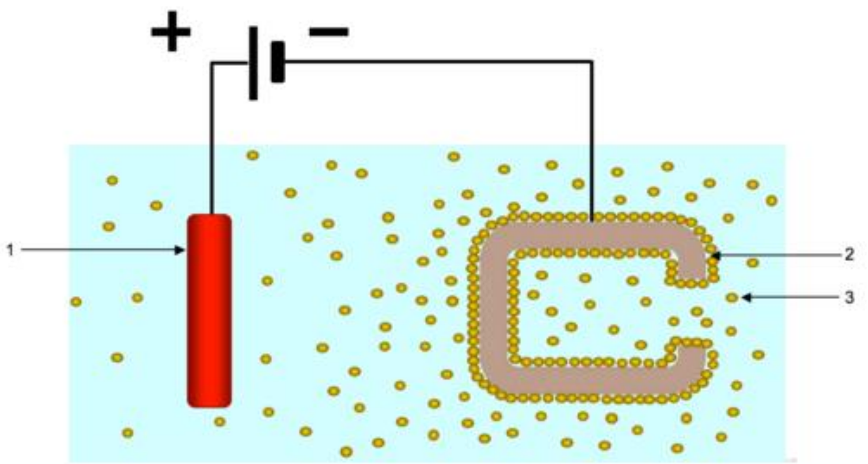
Batteries & Supercaps 2023, 6, e202200441

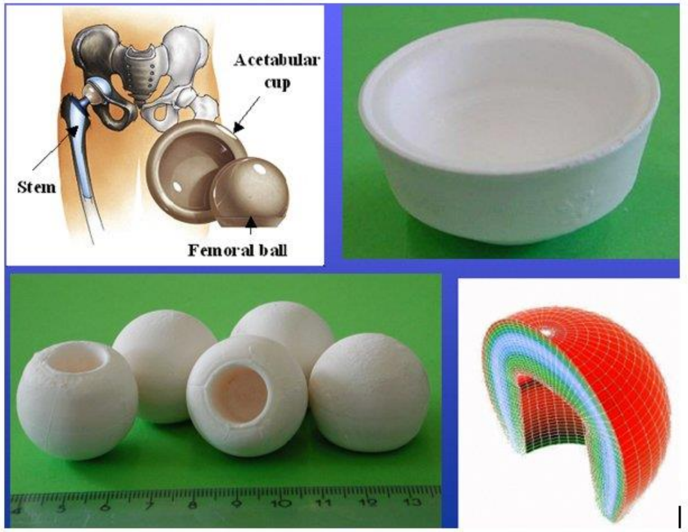


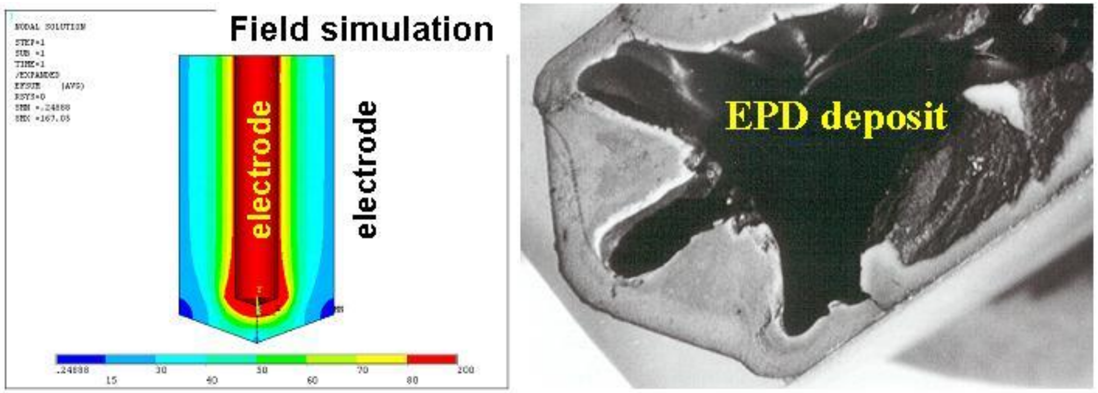
Photographs of a) $LiFePO_4$/Al foam and
b) $Li_4Ti_5O_{12}$\Ni foam electrodes manufactured by EPD.

6) EPD

Complex shaped substrates



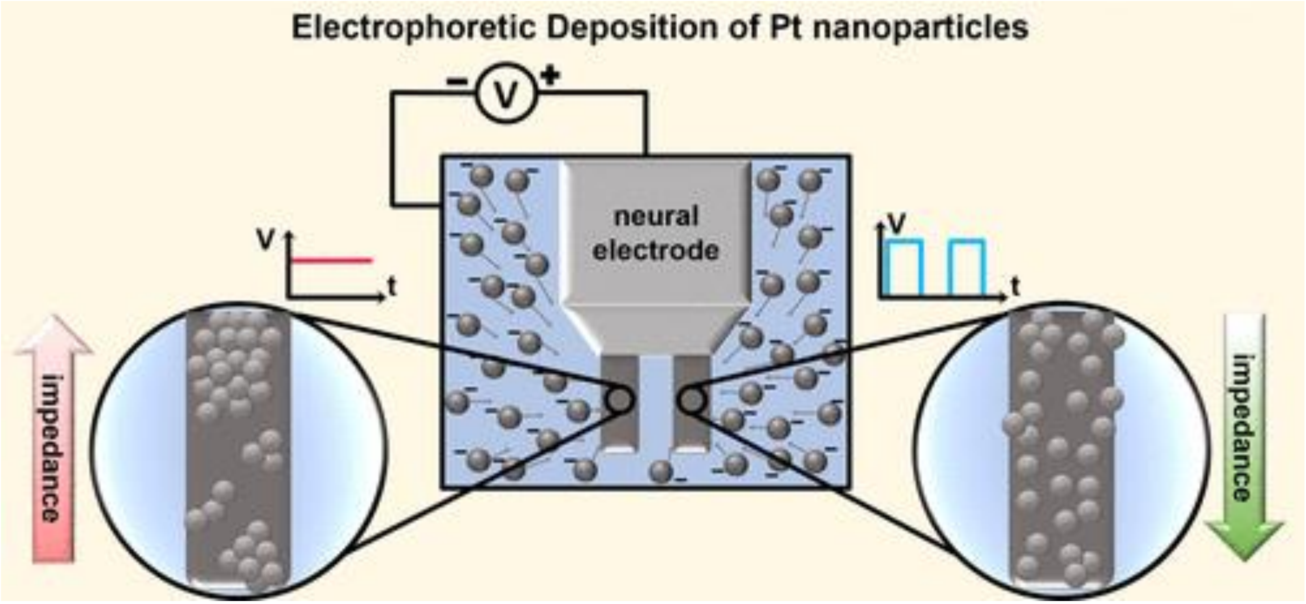


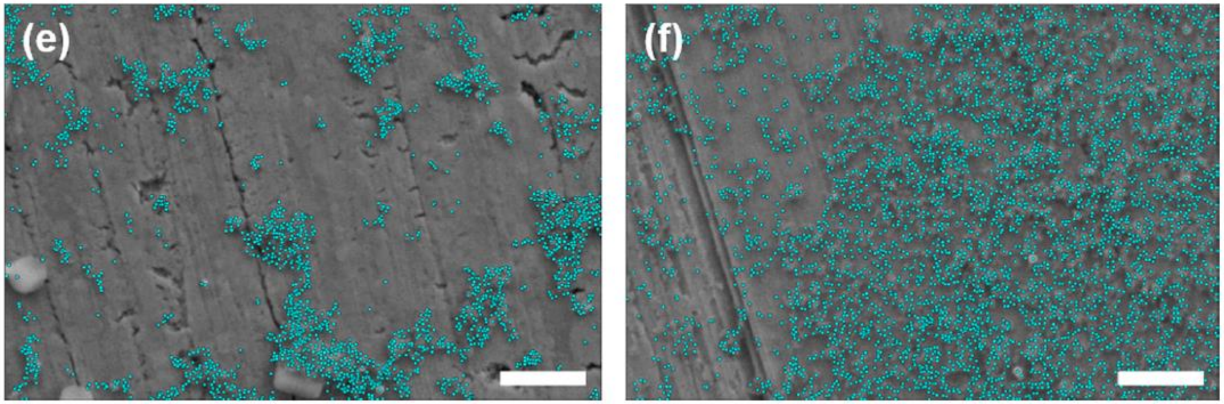


https://www.mtm.kuleuven.be/onderzoek/siem/Ceramics/old-info/epdmodelling

6) EPD

DC versus AC

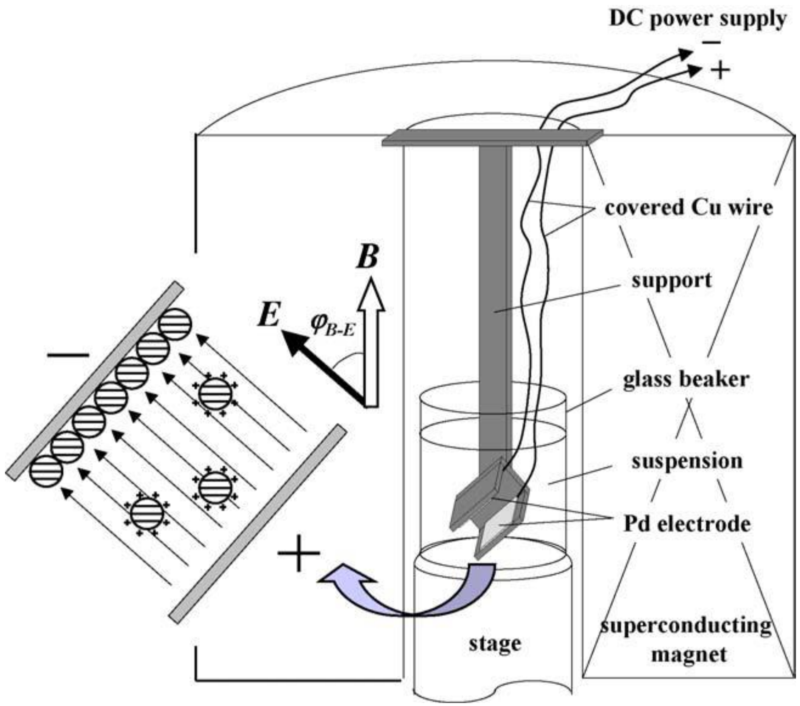




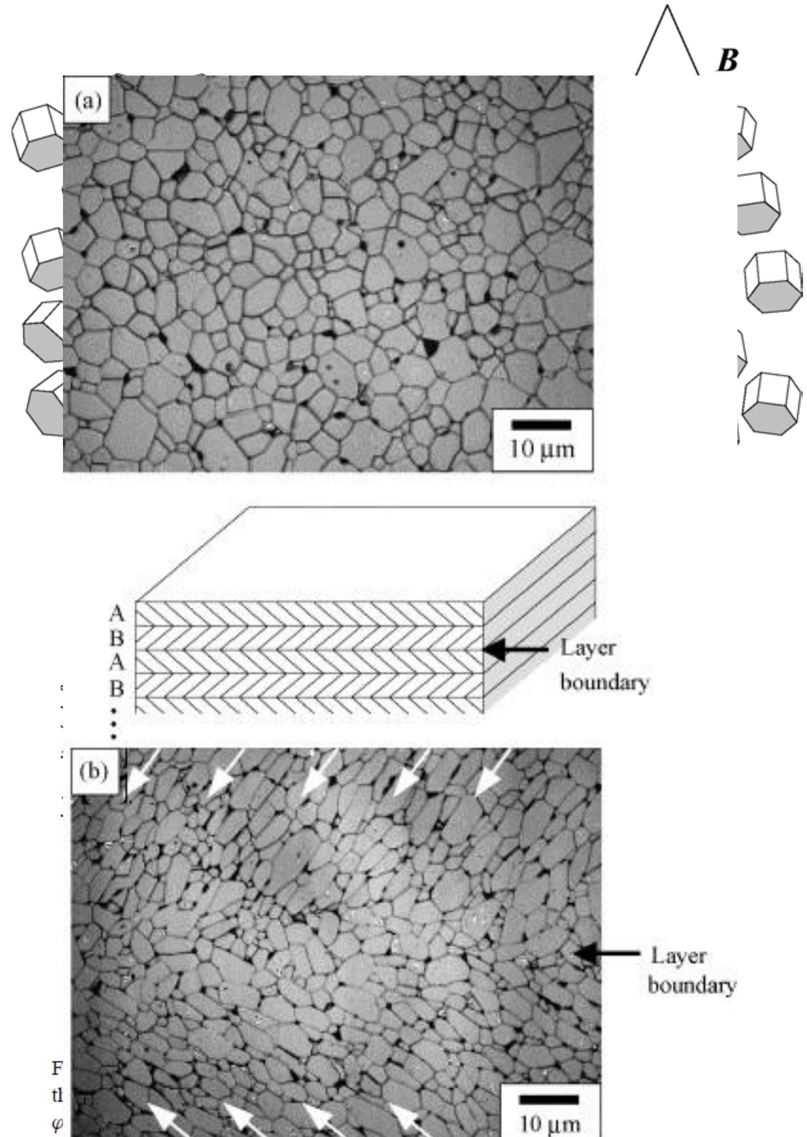
V. Ramseh et al., Langmuir 2021, 37, 9724−9734

6) EPD

Magnetic field assisted EPD



T. Uchikoshi et al., J. Eur. Ceram. Soc., 26 (2006) 559–563
T. Suzuki et al., J. Eur. Ceram. Soc., 26 (2006) 661–665



(hkl) and the basal plane (001) of a tetragonal unit cell of titania are also shown in this figure.

6) EPD

The main advantages:

•Simplicity and very short process,
•Thin and uniform coating,
•Complex shape
•Macroscopic and nano length scales,
•Low cost and energy process,
•Room temperature, ambient pressure.

The main disadvantages:

- Conductive susbtrate (?)

https://www.sbs-zipper.com/blog/usage-of-electrophoresis-in-the-zipper-industry/

https://youtu.be/IedsxsFKoy0

Outline

1) Introduction

2) Spin-Coating

3) Dip-Coating

4) Mayer bare coating

5) Spray-Coating

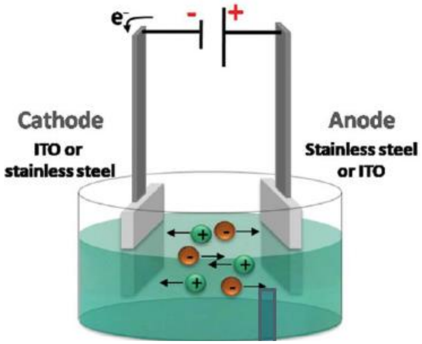
6) EPD

7) Conclusion

7) Conclusion

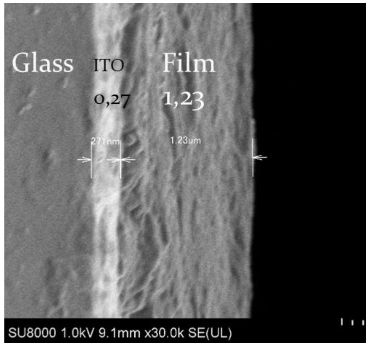
	Spin Coating	Dip Coating	Doctor blade	Spray-coating	EPD
Cost	Low	Low	Low	High	Medium
Scalability	Very limited	Limited	Possible	Possible	Possible
Complexity	Low	Medium	Medium	Low	Low
Uniform thin-films produced?	High	High	Medium	Medium	High
Coatable Surfaces	Small, flat only	Rigid substrates?	Flexible or rigid substrates	Complex, Flexible or rigid substrates	Complex, Flexible or rigid substrates, conductive only.
Solution Wastage	High	Medium	Medium	Low	low

7) Conclusion



Electrophoresis

~100 nm to few microns



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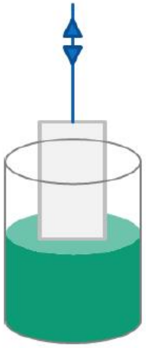
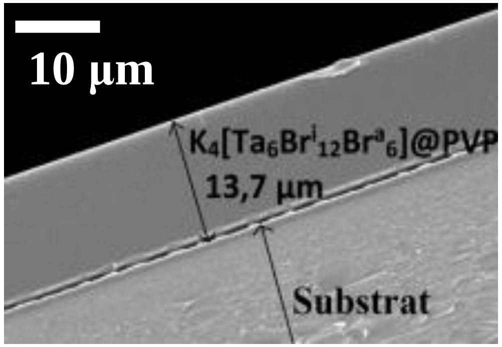
N. Nguyen *et al.*, Bull. Chem. Soc. Jpn, 91, 1763, 2018
N. Nguyen, *et al.* R. Soc. Open Sci., *6*, 181647, 2019

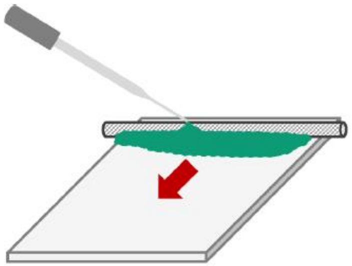


Dip coating

~10-20 microns

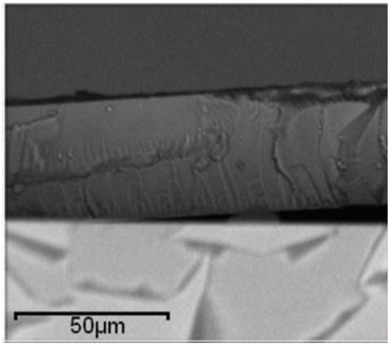


T. Aubert *et al.*, Part. Part. Syst. Charact., 30, 90, 2013
G. Truong *et al.*, Sci. Tech. Adv. Mater., 17:1, 443, 2016
A. Renaud, *et al.*, J. Mater. Chem. C, 5, 8160, 2017



Mayer bar coating

~up to 100 microns



C. Lebastard, et al., ACS Appl. Mater. Interfaces, 14, 21116, 2022
C. Lebastard, *et al.*, Nanomaterials, 12, 2052, 2022
C. Lebastard, *et al.*, Sci. Technol. Adv. Mater., 23(1), 446, 2022

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ISBN 978-3-211-99311-8 (eBook)

-Electrophoretic Deposition of Nanomaterials, DOI 10.1007/978-1-4419-9730-2
ISBN 978-1-4419-9730-2 (eBook)

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-D. Grosso, How to exploit the full potential of the dip-coating process to better control film formation, J. Mater. Chem., 2011, 21, 17033–17038

-E. Rio et al., Withdrawing a solid from a bath: how much liquid is coated?
Advances in Colloid and Interface Science, 247, 100-114, 2017

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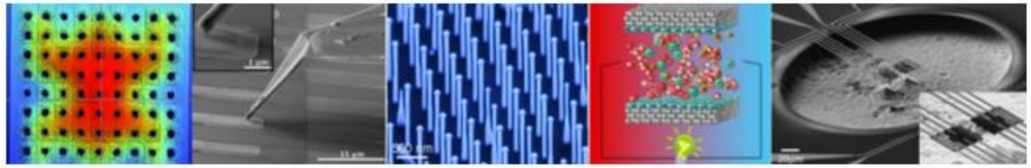
GDR NAnoMaterials for Energy applications



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Rennes, Campus de Beaulieu

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https://gdr-name-2023.sciencesconf.org/

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Jacky Even
INSA, Rennes

Vincent Artero
CEA, Grenoble

Damien Voiry
IEM, Montpellier

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Limite de soumission des résumés
Limite d'inscription

140 personnes max

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Thank you for your attention

Merci beaucoup

どうもありがとうございます

Fabien Grasset

13th June 2023, EI NANO