



Synthesis of Materials for Energy Storage and Conversion

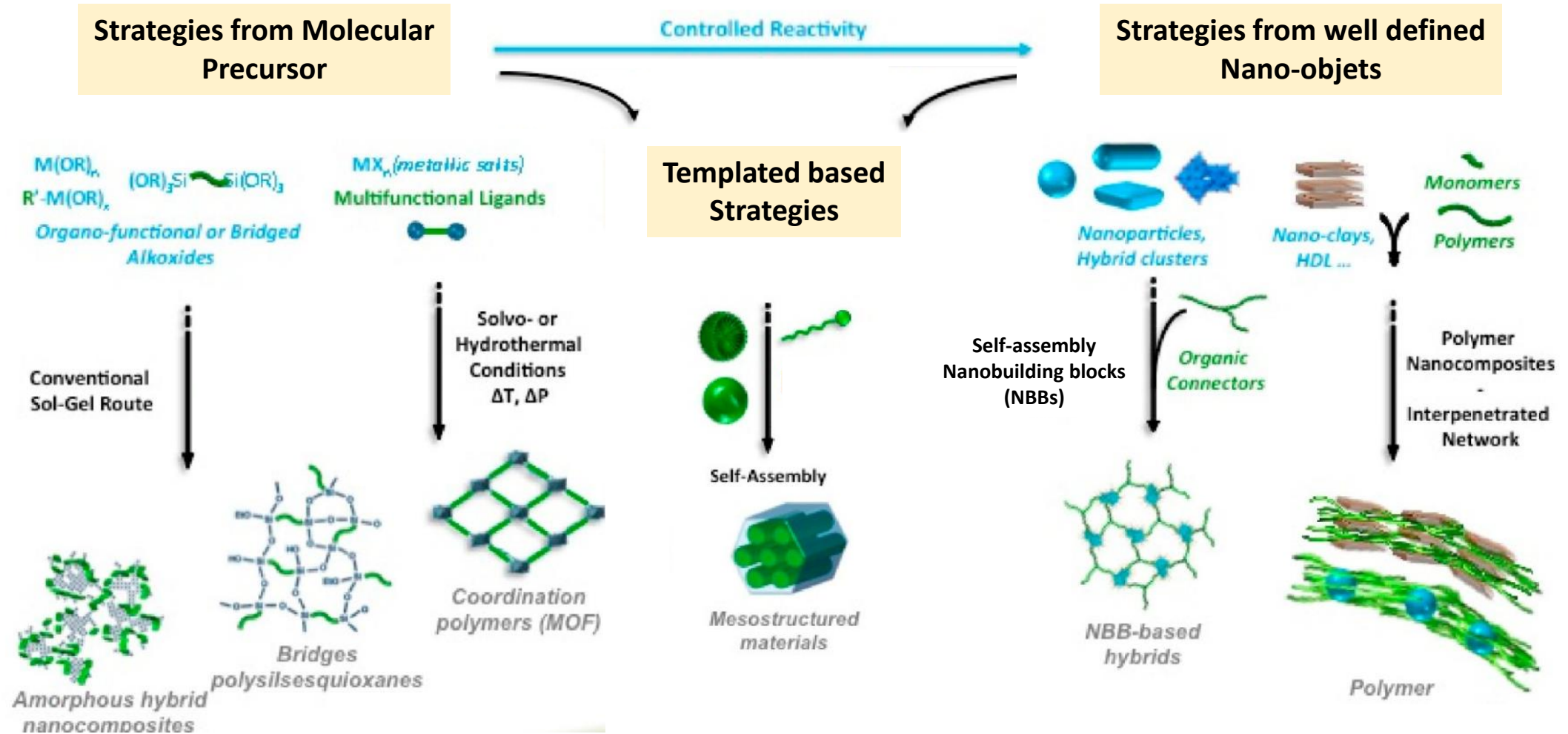
C. Laberty-Robert

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Sorbonne-Université- UMR7574

christel.laberty@sorbonne-universite.fr

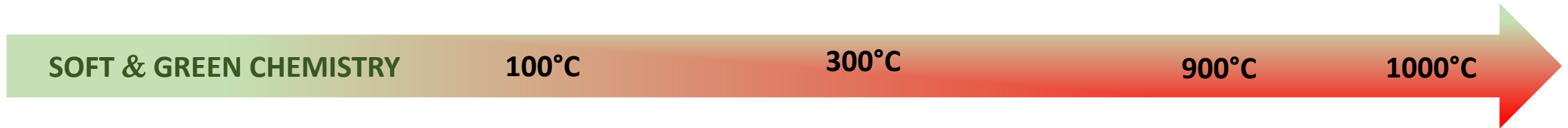
Rational Strategies for the Controlled Synthesis of Nanoparticles



Materials Processing : Casting, Electrospinning, dip-, spin-, spray-coating, soft lithography, spray drying,...

Experimental Levers :

Temperature, Time, surface complexants, solvent composition, pH, ionic strength,...



SOFT & GREEN CHEMISTRY

100°C

300°C

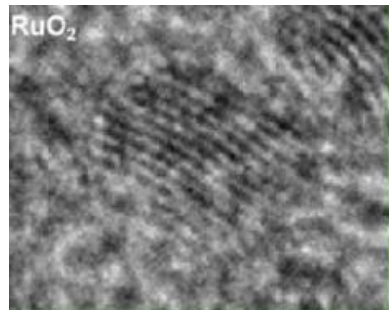
900°C

1000°C

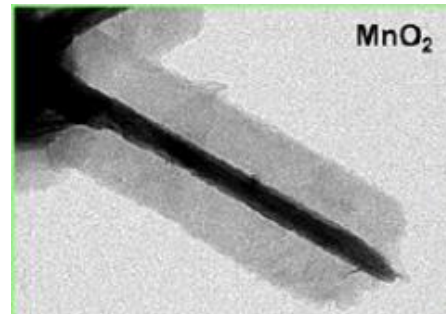
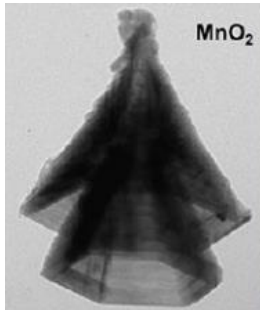
MILD CONDITIONS (atmospheric pressure)

Aqueous precipitation

Self-assembly



**Classical
Crystallization**



**Heterogeneous
nucleation**

Rational Strategies for the controlled synthesis of nanoparticles : Crystal Structure, Morphology, Size, and heterostructure

SOFT & GREEN CHEMISTRY

100°C

300°C

900°C

1000°C

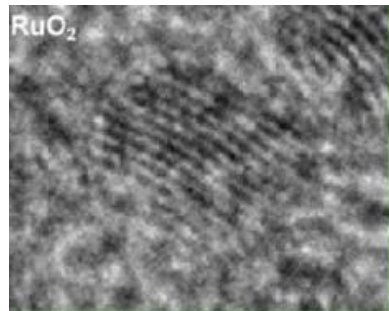
MILD CONDITIONS (atmospheric pressure)

Aqueous precipitation

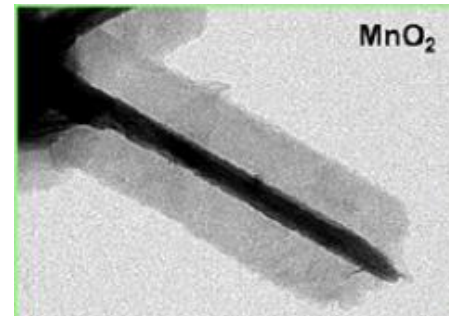
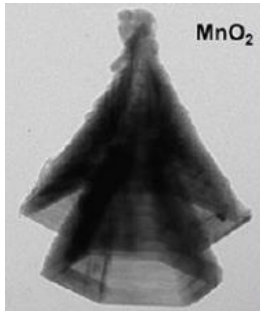
Precursor choice for
colloidal routes

Self-assembly

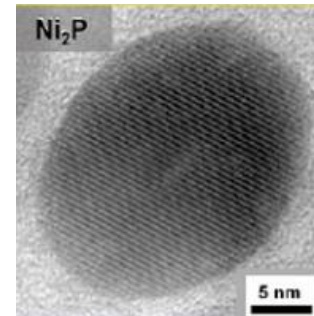
Precursor –based strategy



Classical
Crystallization



Heterogeneous
nucleation



Rational Strategies for the controlled synthesis of nanoparticles: Crystal Structure, Morphology, Size, and heterostructure

SOFT & GREEN CHEMISTRY

100°C

300°C

900°C

1000°C

MILD CONDITIONS (atmospheric pressure)

Aqueous precipitation

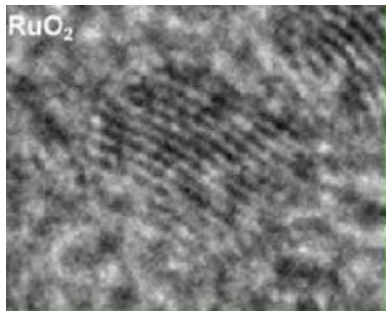
Self-assembly

**Precursor choice for
colloidal routes**

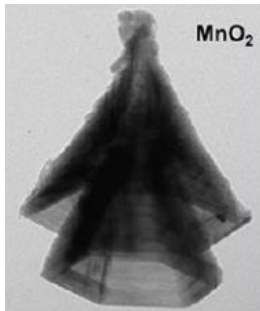
Precursor –based strategy

**Alternatives solvents for
colloidal routes**

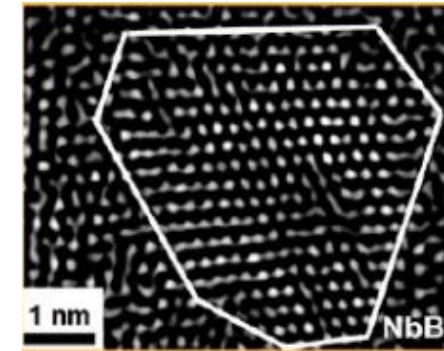
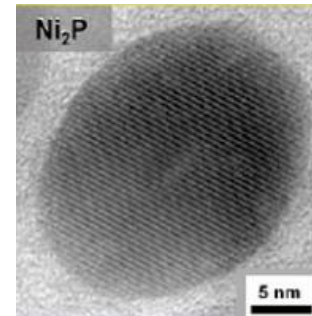
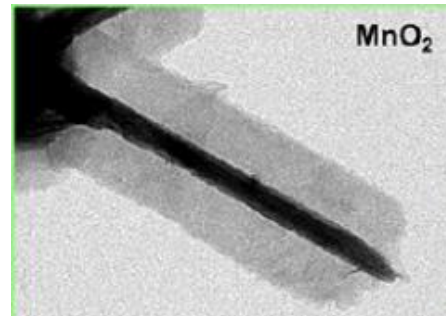
Solvent –based strategy



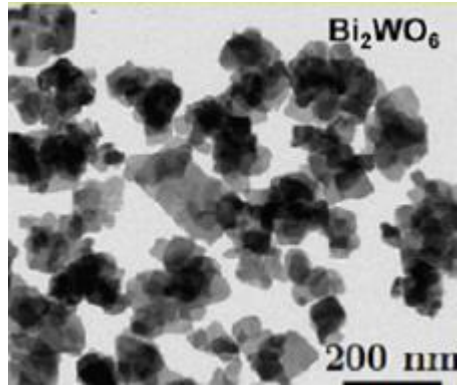
**Classical
Crystallization**



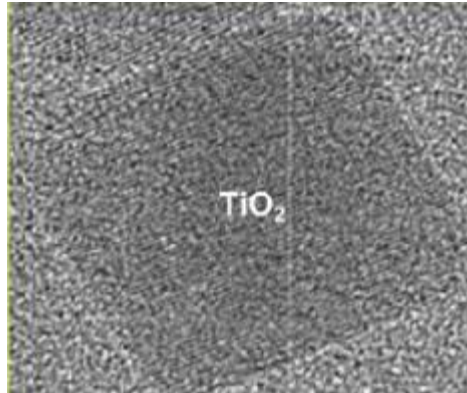
**Heterogeneous
nucleation**



Microwave Heating



Convection Heating



Heating Process

SOLVOTHERMAL CONDITIONS

SOFT & GREEN CHEMISTRY

100°C

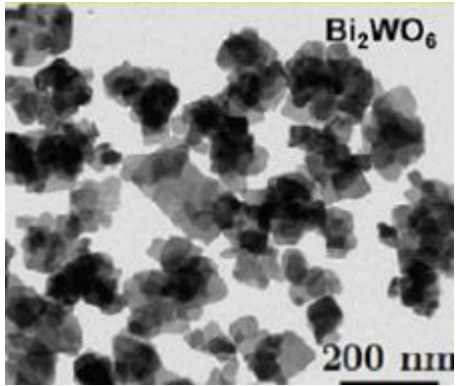
300°C

900°C

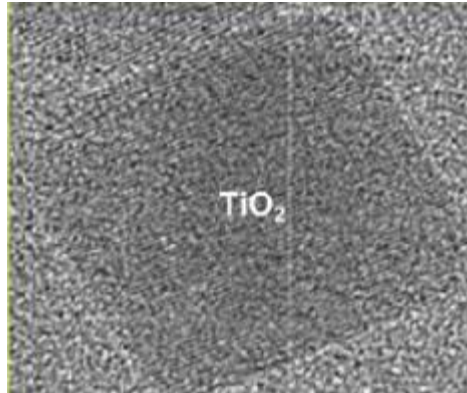
1000°C

Rational Strategies for the controlled synthesis of nanoparticles

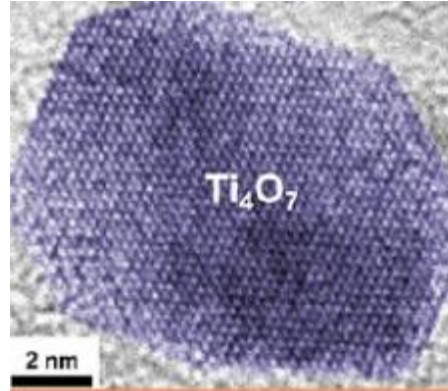
Microwave Heating



Convection Heating



Precursor-based & Process-based strategy



Heating Process

Sol-gel routes for carbothermal syntheses

SOLVOTHERMAL CONDITIONS

TWO-STEP LOW- HIGH TEMPERATURES

SOFT & GREEN CHEMISTRY

100°C

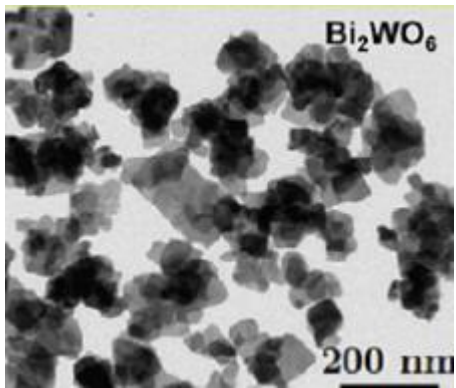
300°C

900°C

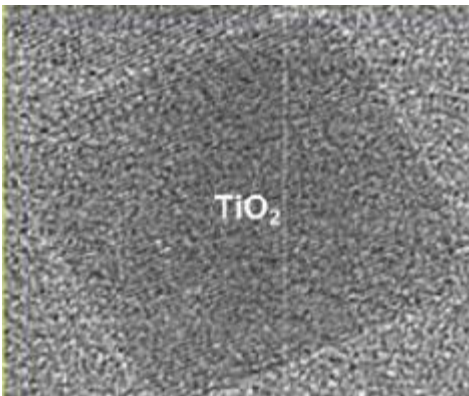
1000°C

Rational Strategies for the controlled synthesis of nanoparticles

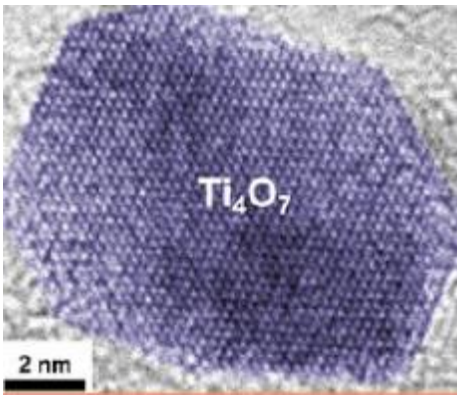
Microwave Heating



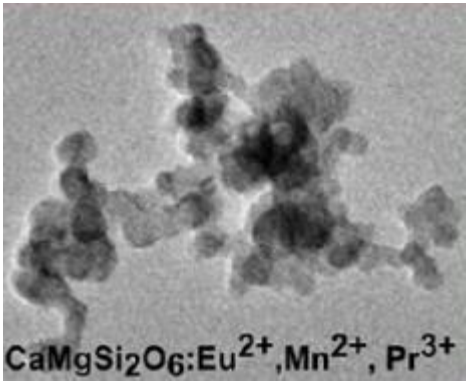
Convection Heating



Precursor-based
&
Process-based strategy



Two steps sol-gel
&
Crystallization Strategy



Heating Process

Sol-gel routes
for carbothermal syntheses

Doping

SOLVOTHERMAL CONDITIONS

TWO-STEP LOW- HIGH TEMPERATURES

SOFT & GREEN CHEMISTRY

100°C

300°C

900°C

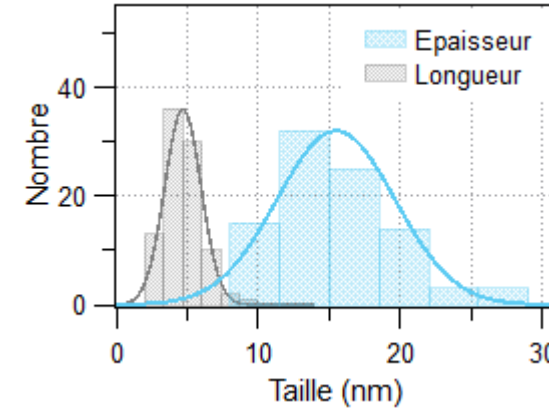
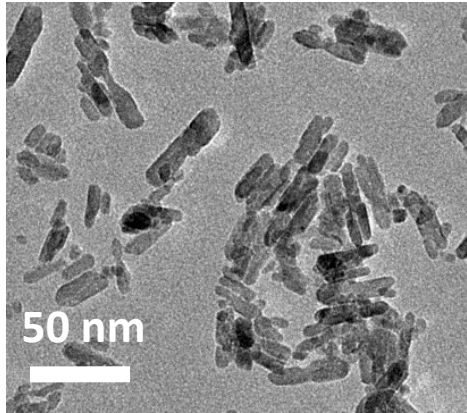
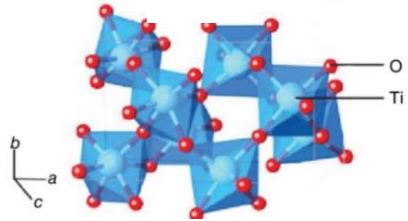
1000°C

Controlling the structure of TiO₂ via the SOLVOTHERMAL approach

Brookite B2



TiCl₄ / TiCl₃
0,2 M / 0,1 M
NaOH (pH = 4.5)
60 °C 1 week



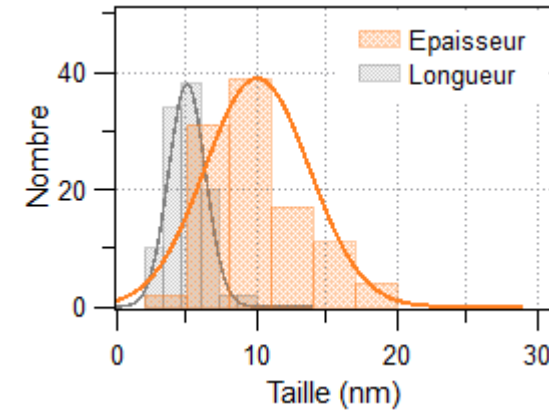
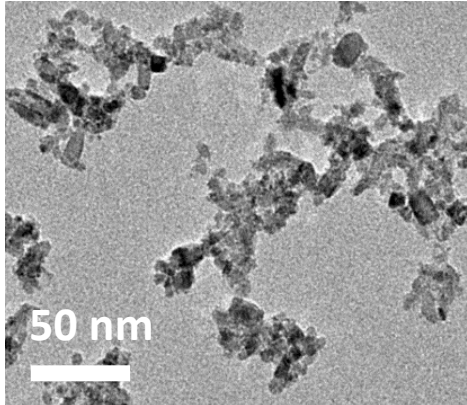
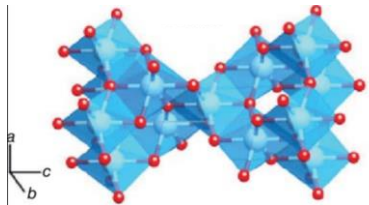
$l = 15.5 \text{ nm} \pm 4.1 \text{ nm}$
 $e = 4.7 \text{ nm} \pm 1.3 \text{ nm}$

Anatase A2



TiCl₄ 0,5 M
NaOH (pH = 6)

Microwave
200 °C 2 h

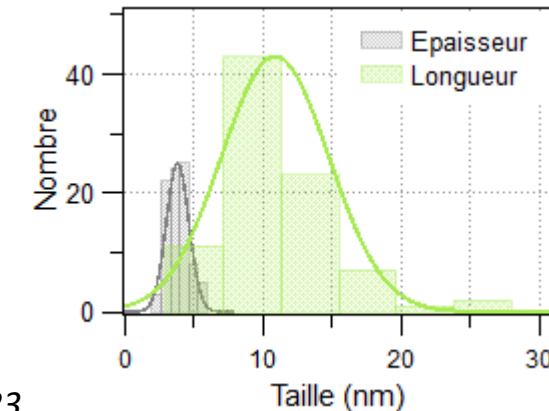
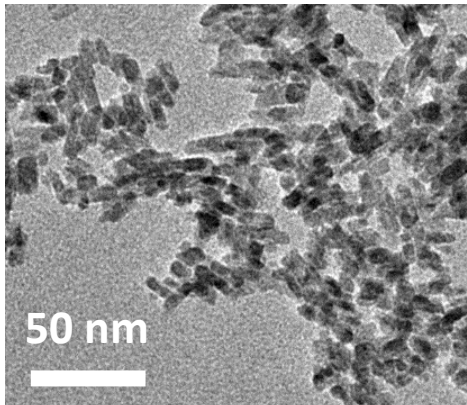
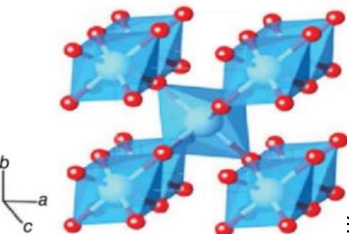


$l = 10.1 \text{ nm} \pm 3.7 \text{ nm}$
 $e = 5.1 \text{ nm} \pm 1.3 \text{ nm}$

Rutile R2



TiCl₃ 0,15 M
NaOH (pH = 4)
70 °C 72 h

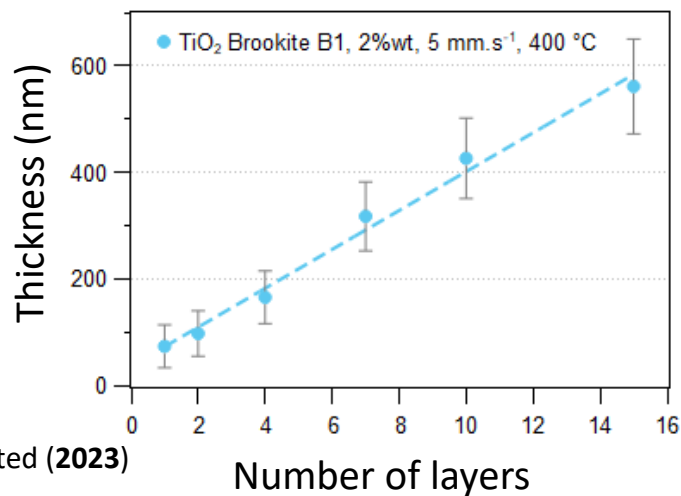
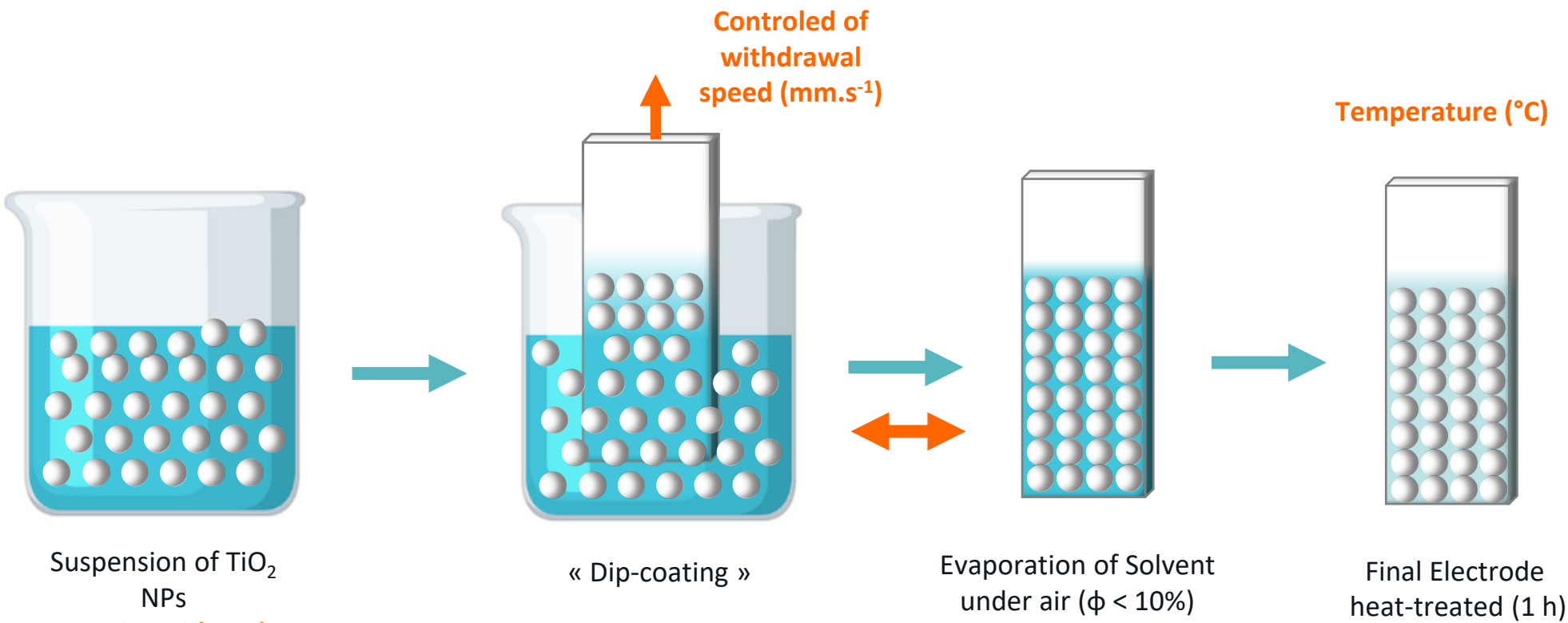


$l = 10.9 \text{ nm} \pm 3.9 \text{ nm}$
 $e = 3.9 \text{ nm} \pm 0.8 \text{ nm}$

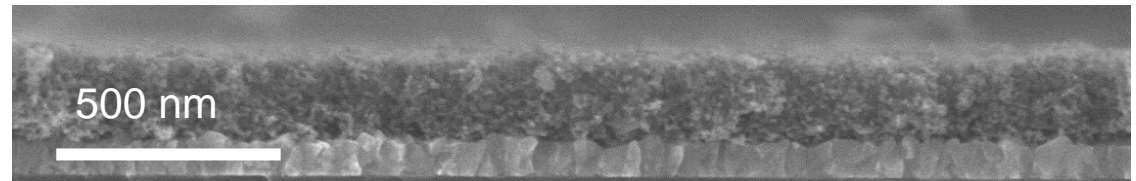
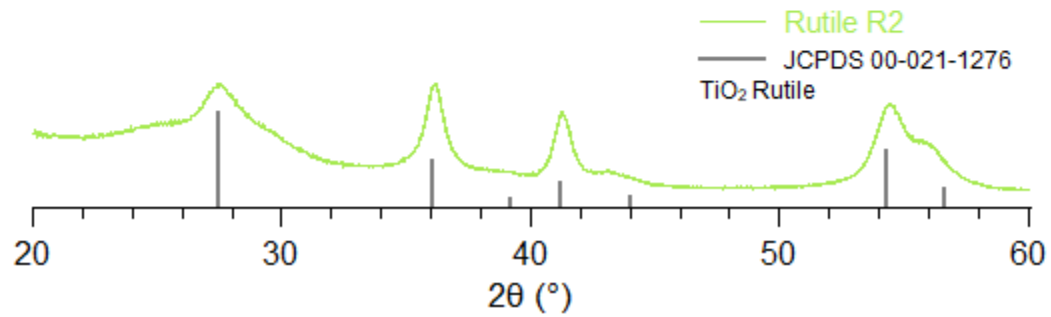
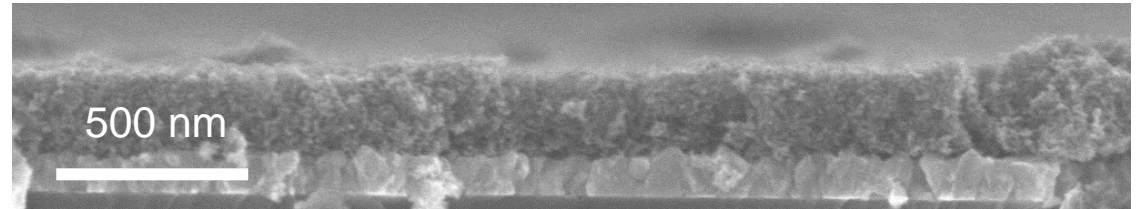
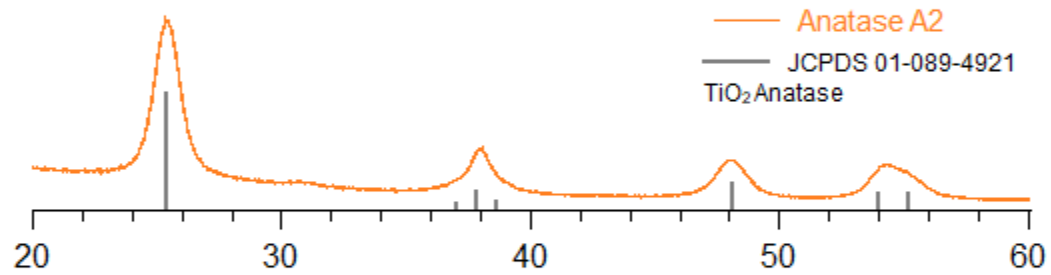
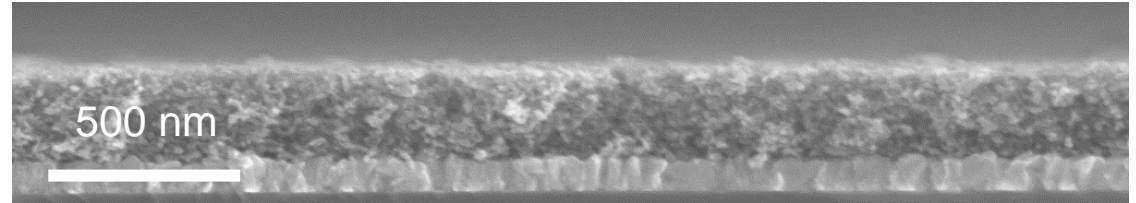
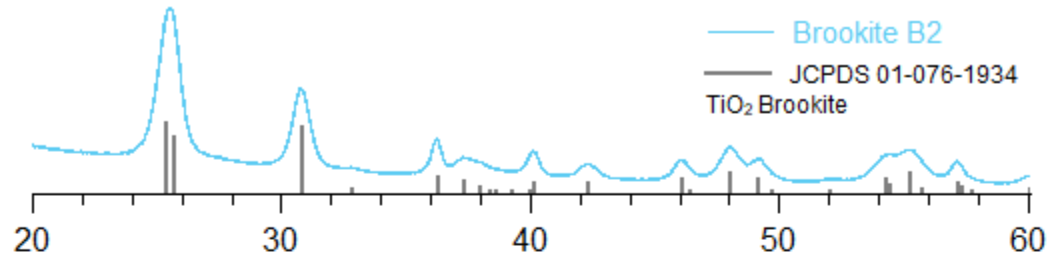
submitted (2023)

El-Nano – Aussois- Juin 2023

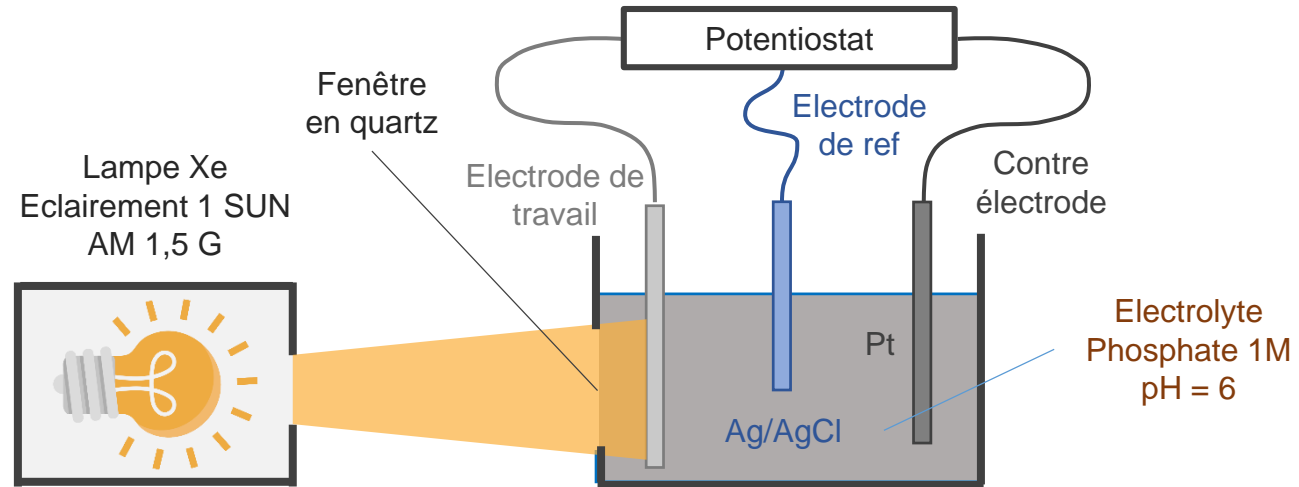
How to assemble the TiO₂ Nanoparticles: Use the dip-coating technique



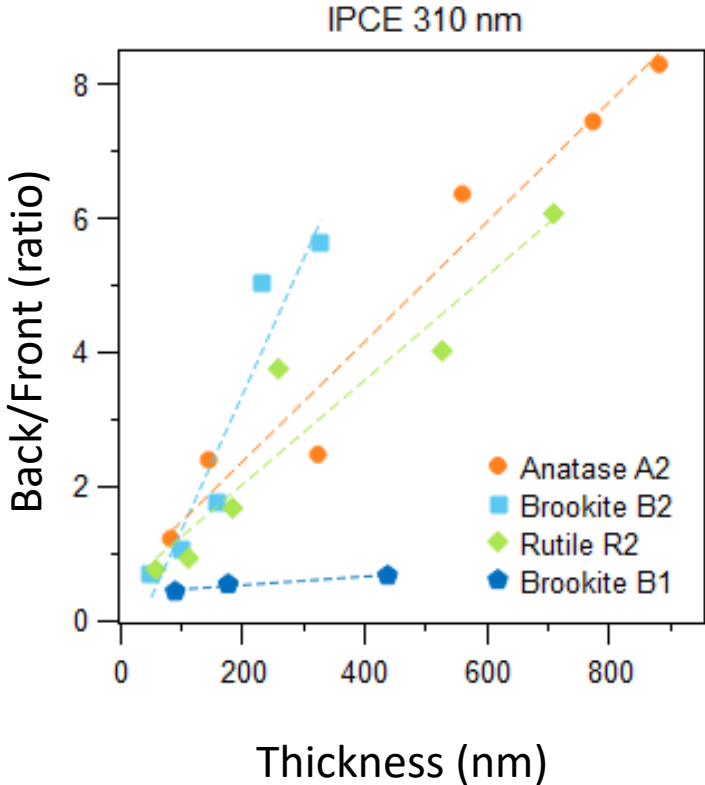
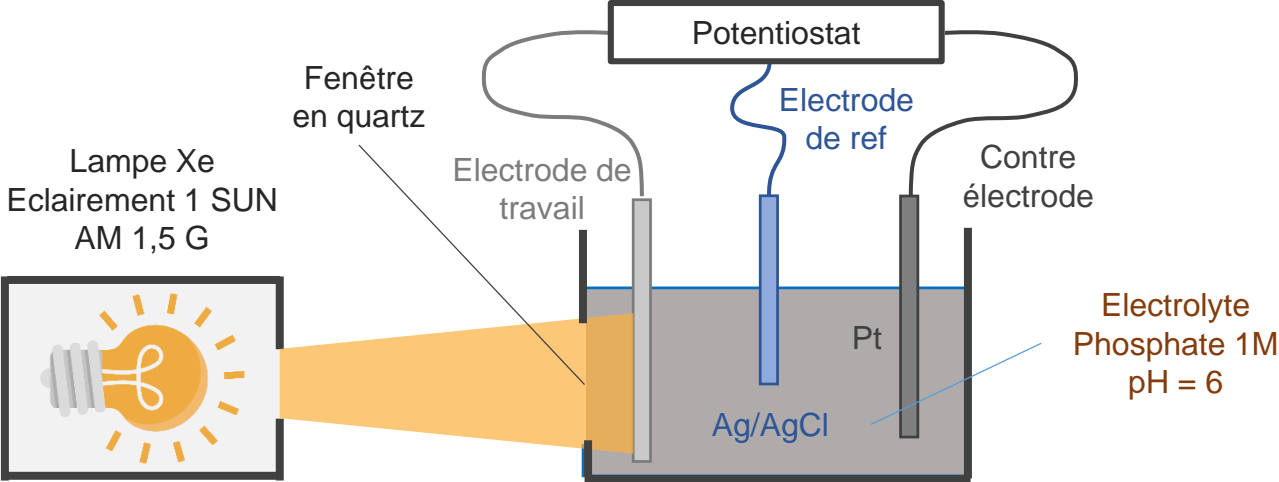
Keeping the Structure of the Bulding Block NPs



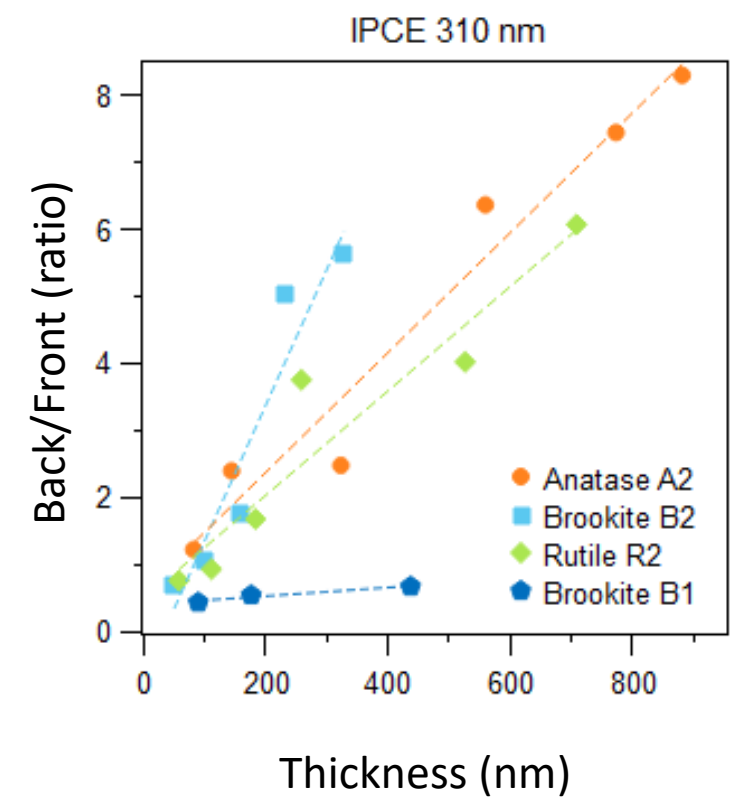
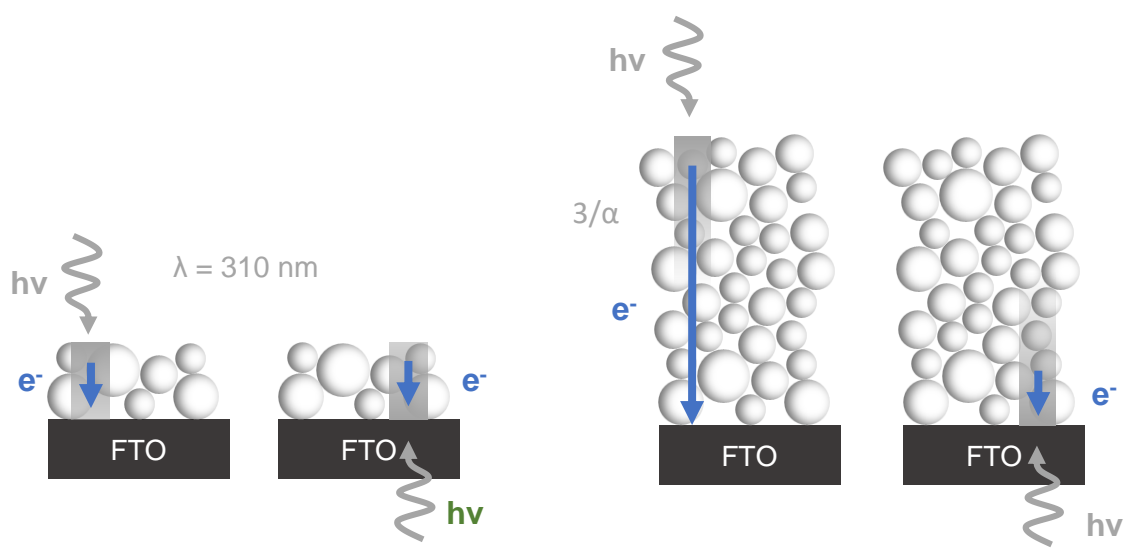
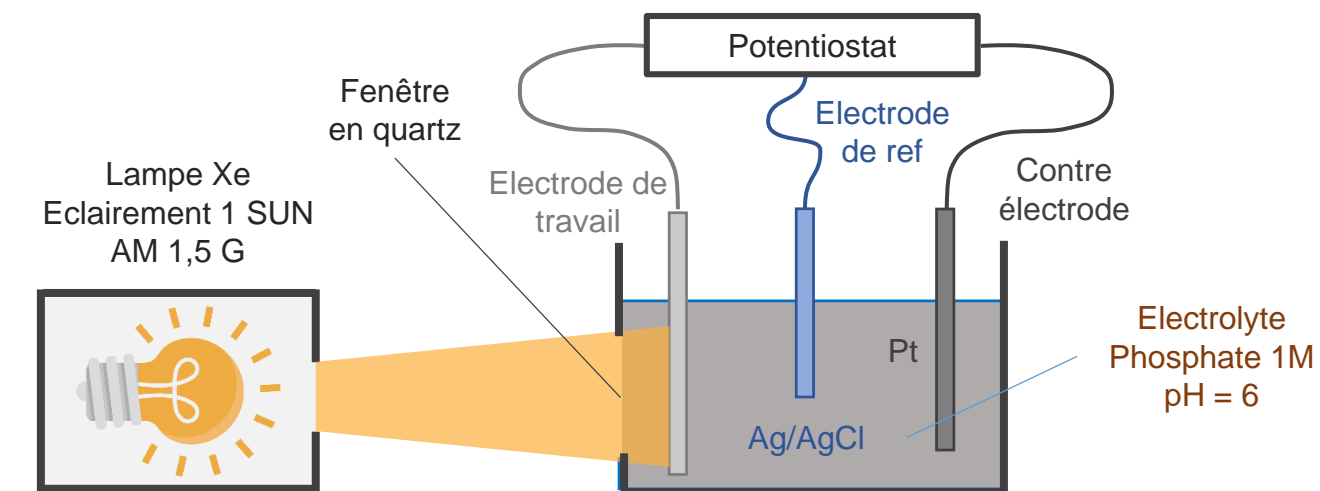
Necessity to Tune the Particle-Particle Contact



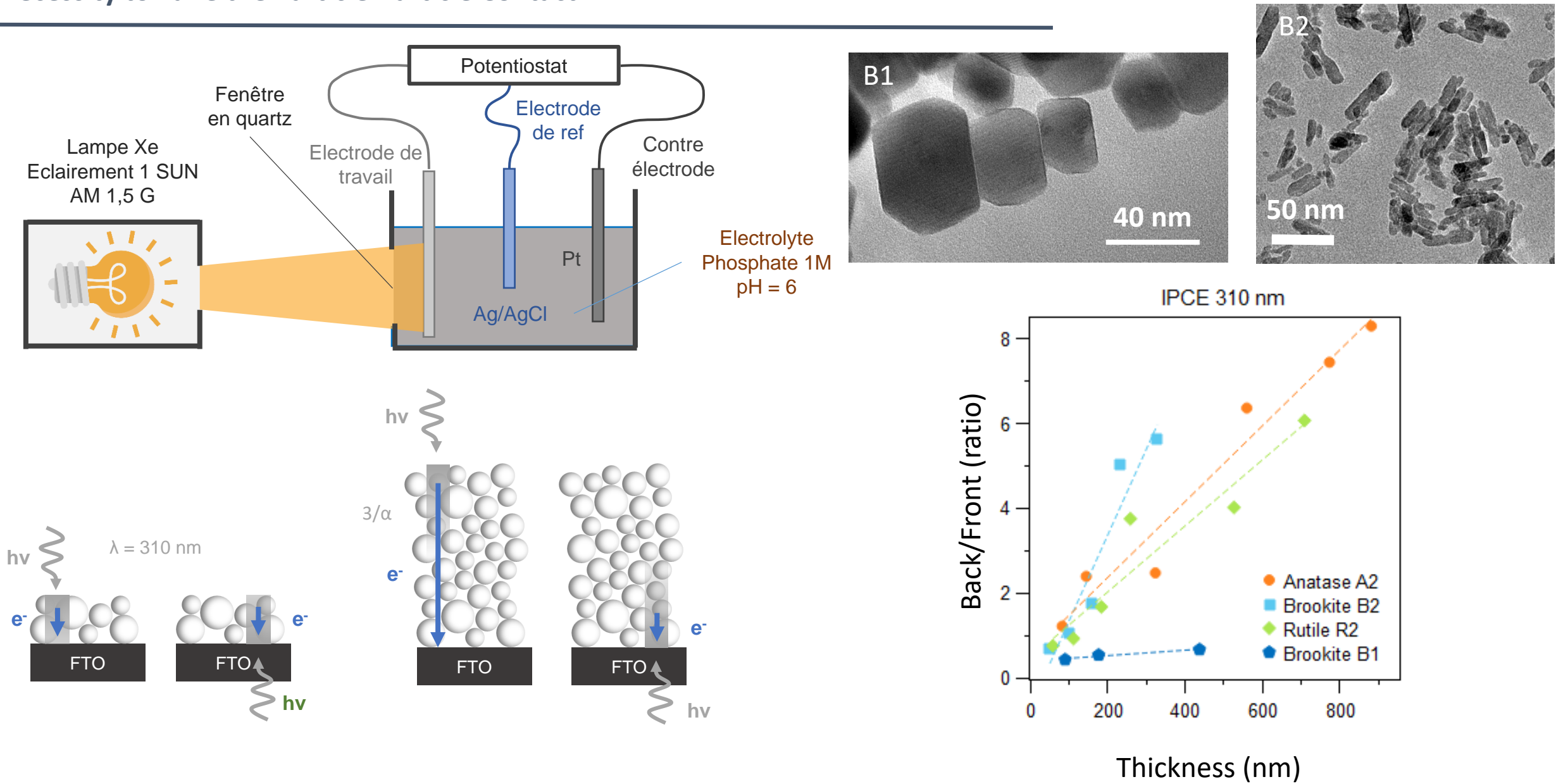
Necessity to Tune the Particle-Particle Contact



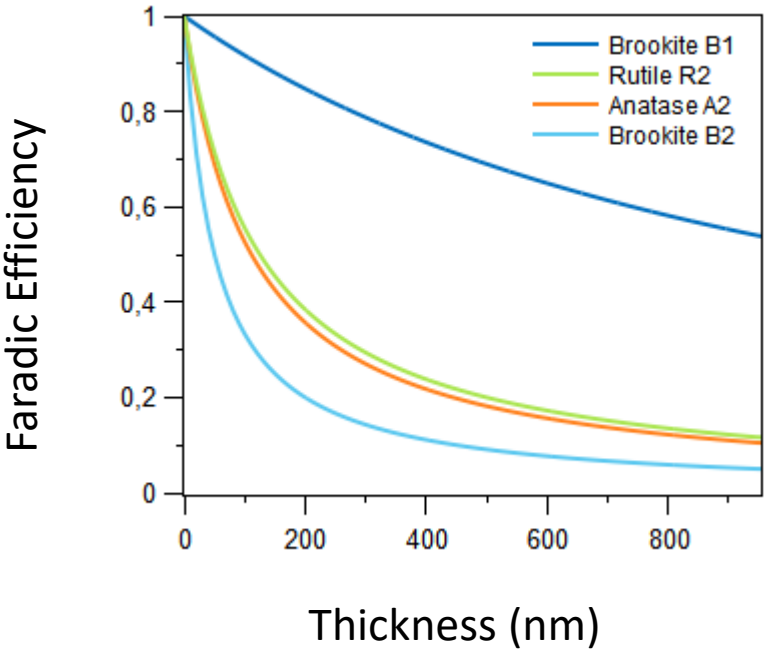
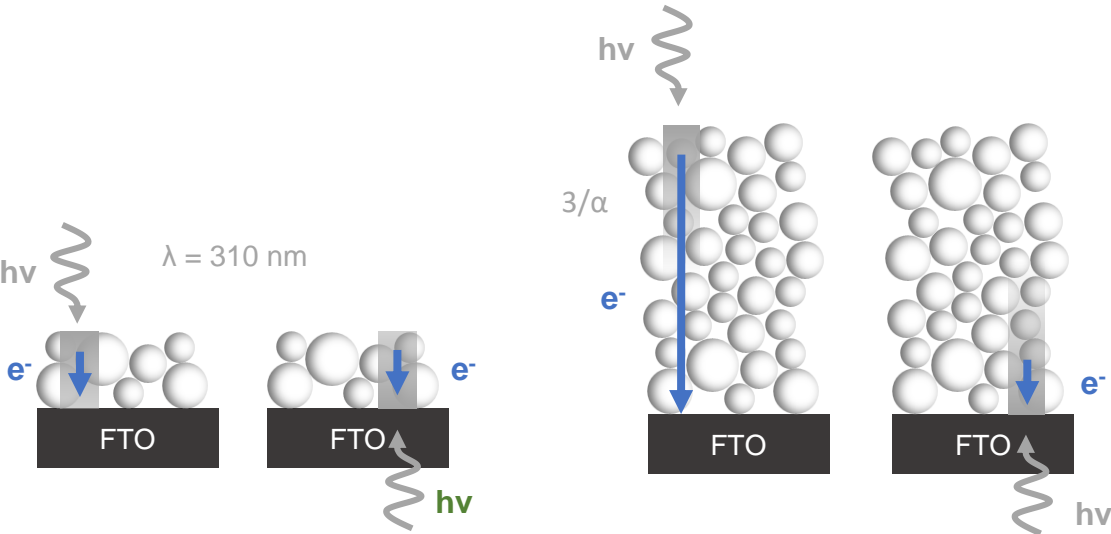
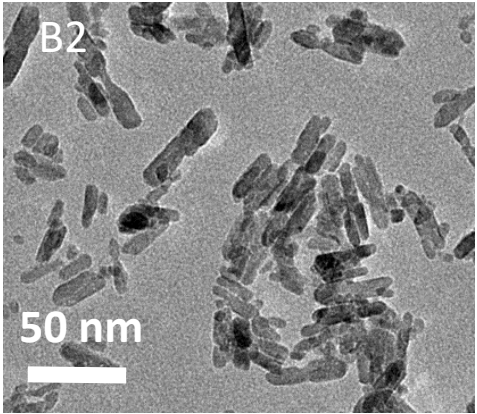
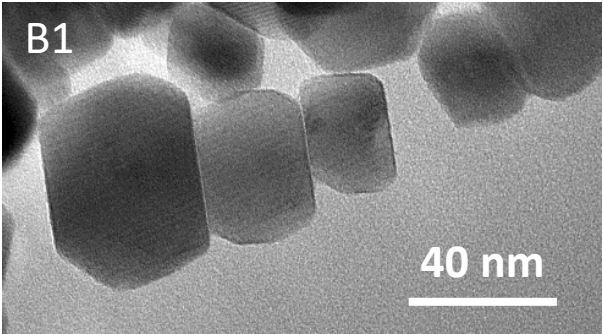
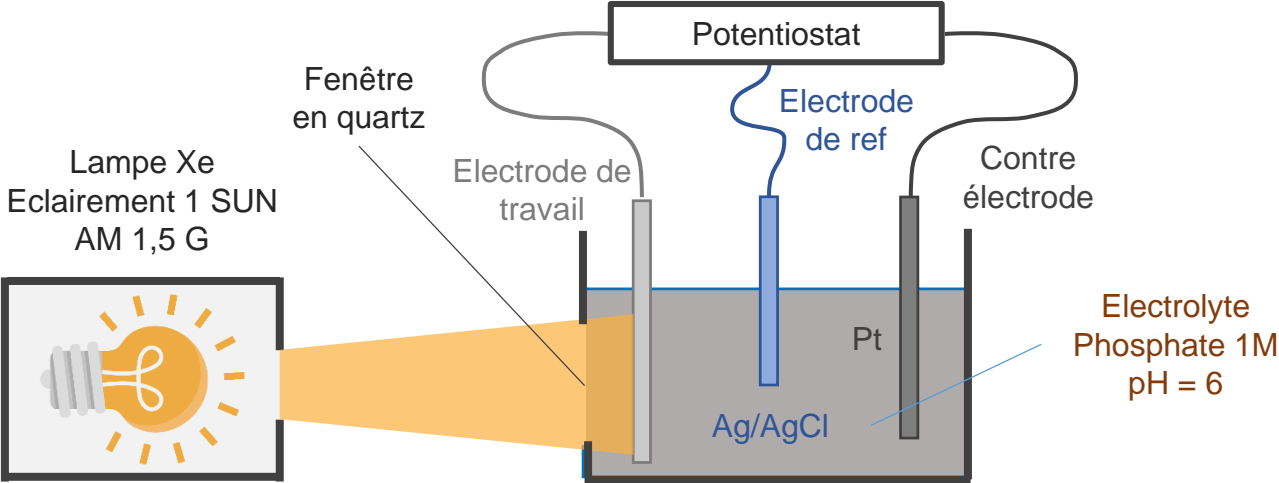
Necessity to Tune the Particle-Particle Contact



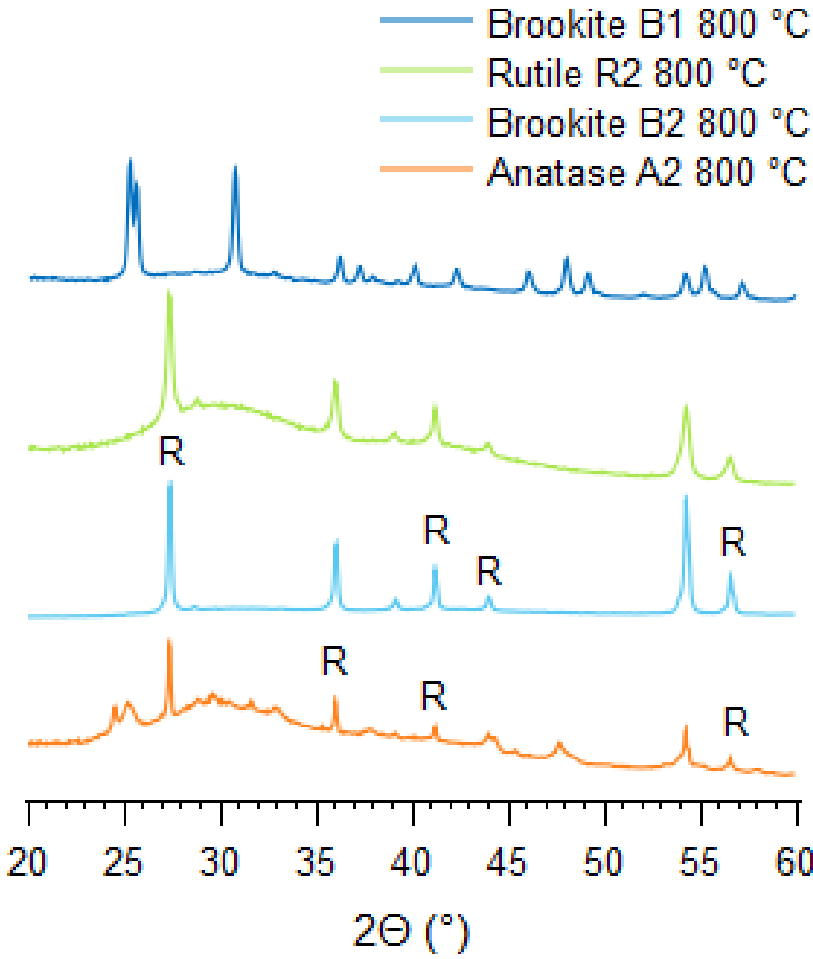
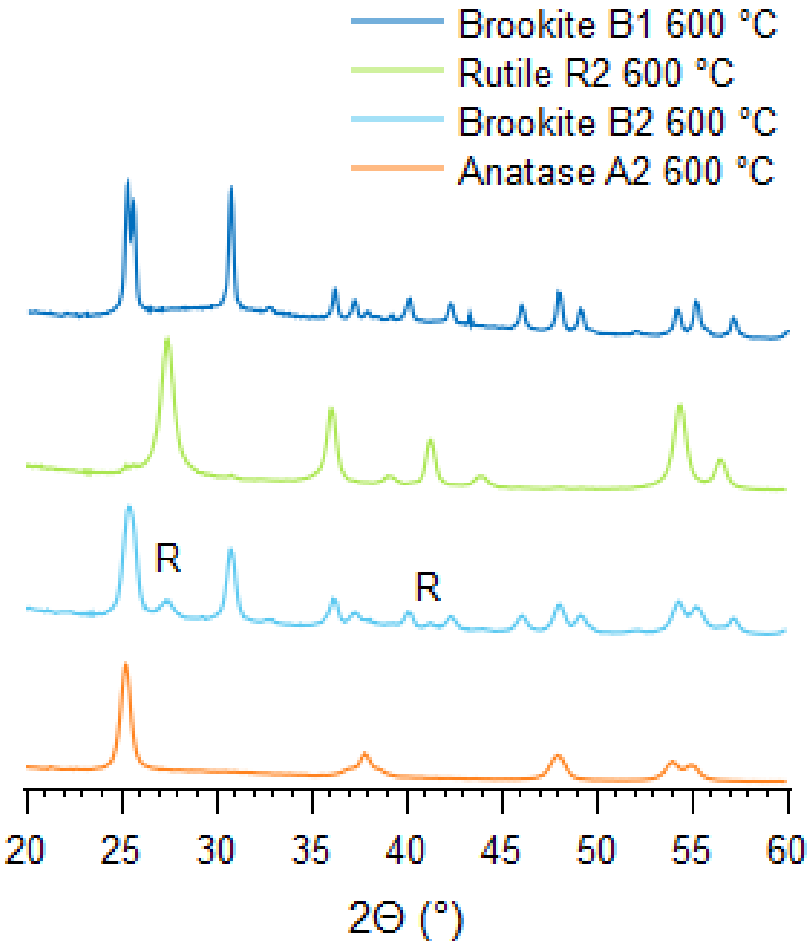
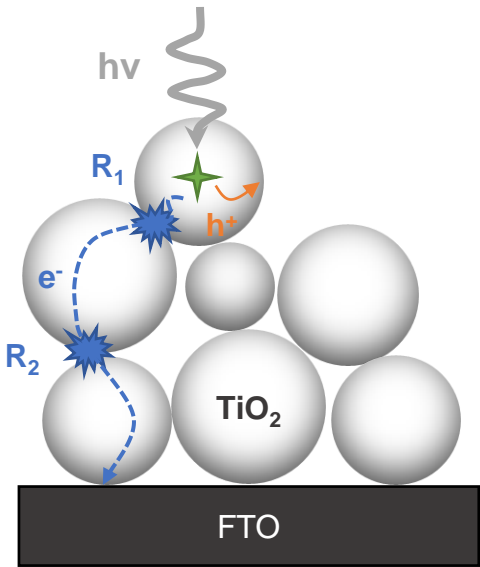
Necessity to Tune the Particle-Particle Contact



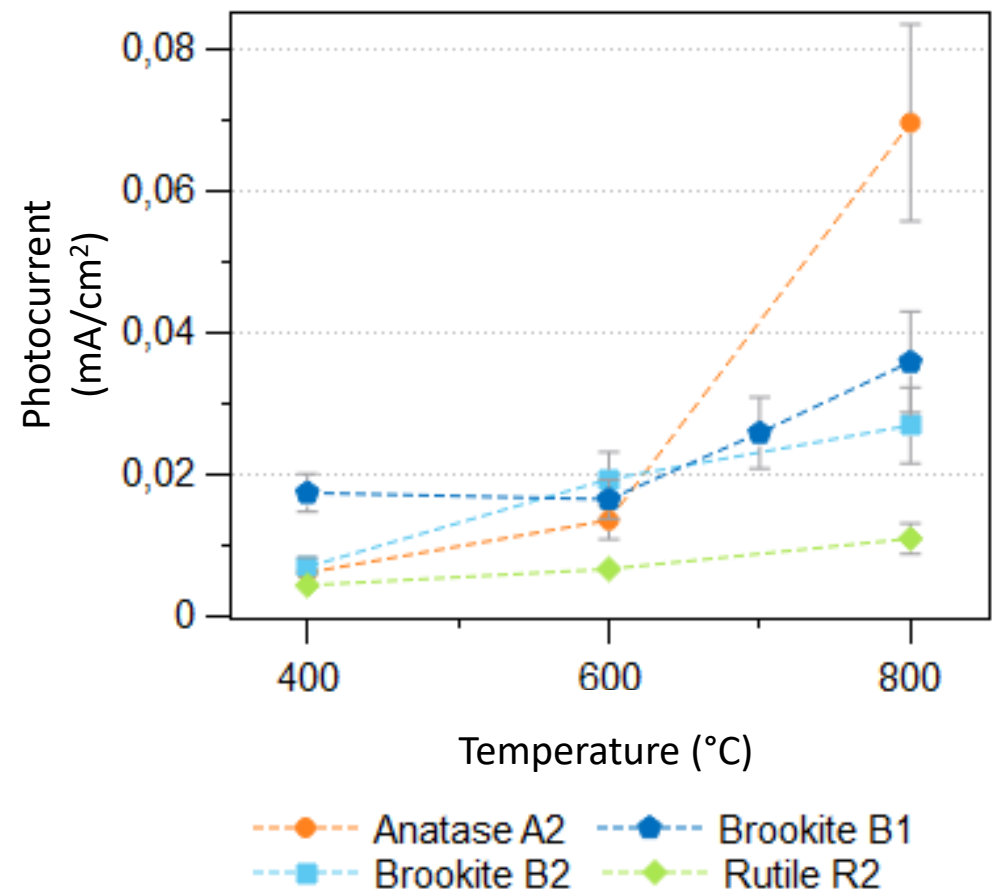
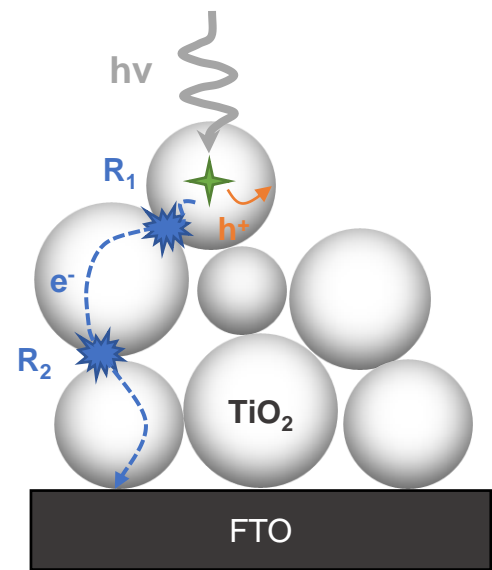
Necessity to Tune the Particle-Particle Contact



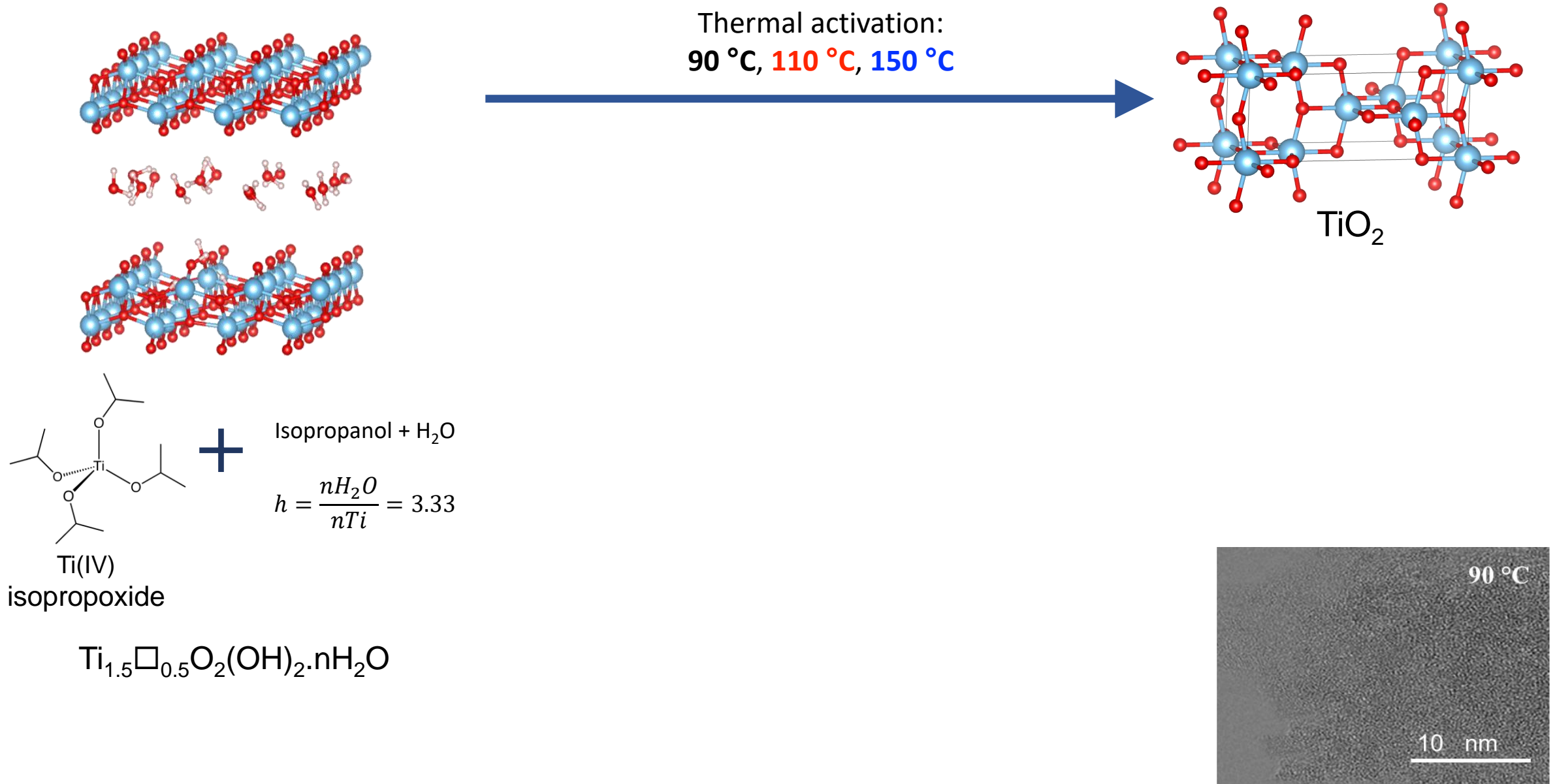
Necessity to Tune the Particle-Particle Contact : Heat Treatment



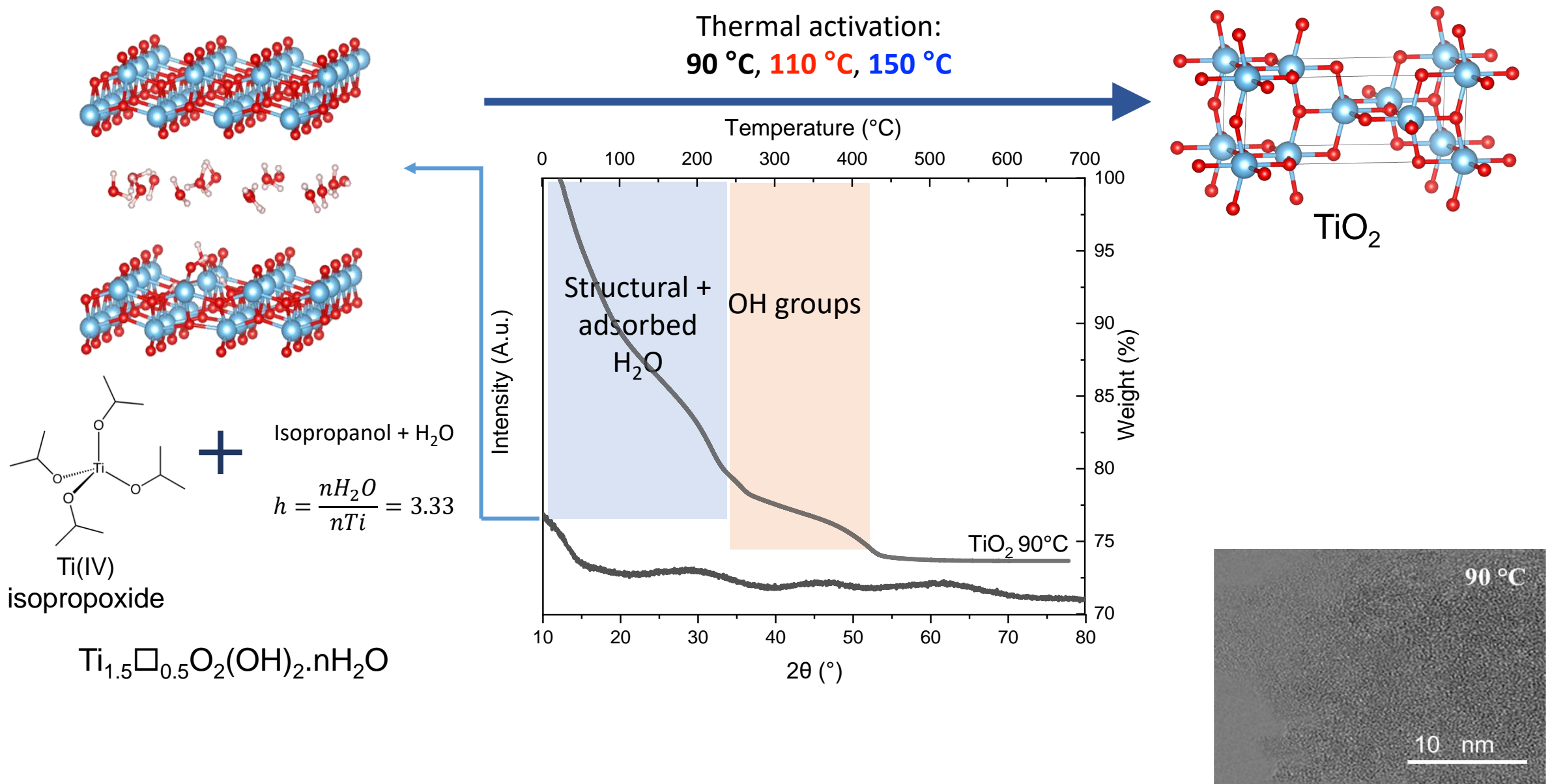
Necessity to Tune the Particle-Particle Contact : Heat Treatment



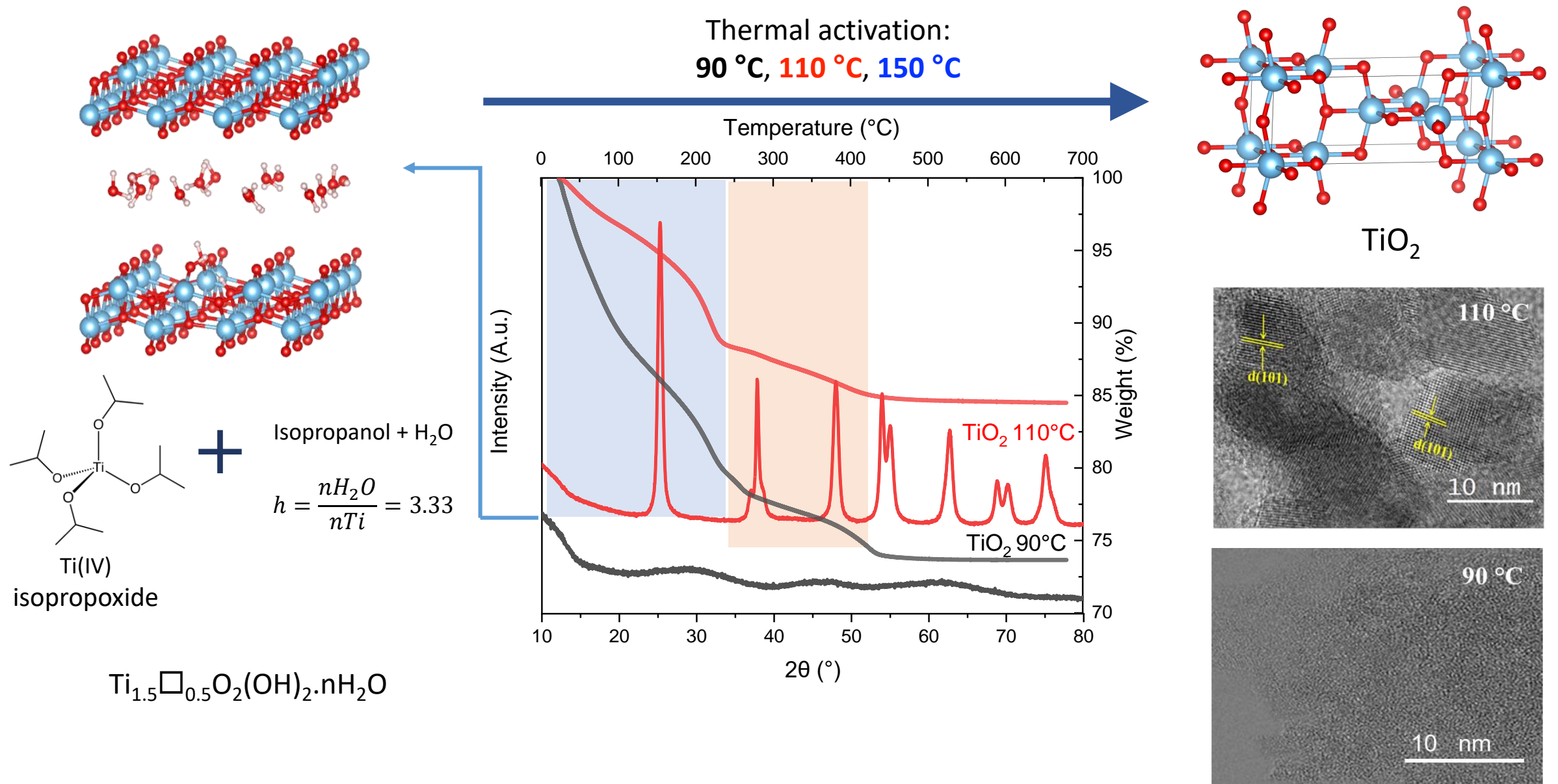
Controlling the structure of TiO₂ via the SOLVOTHERMAL approach



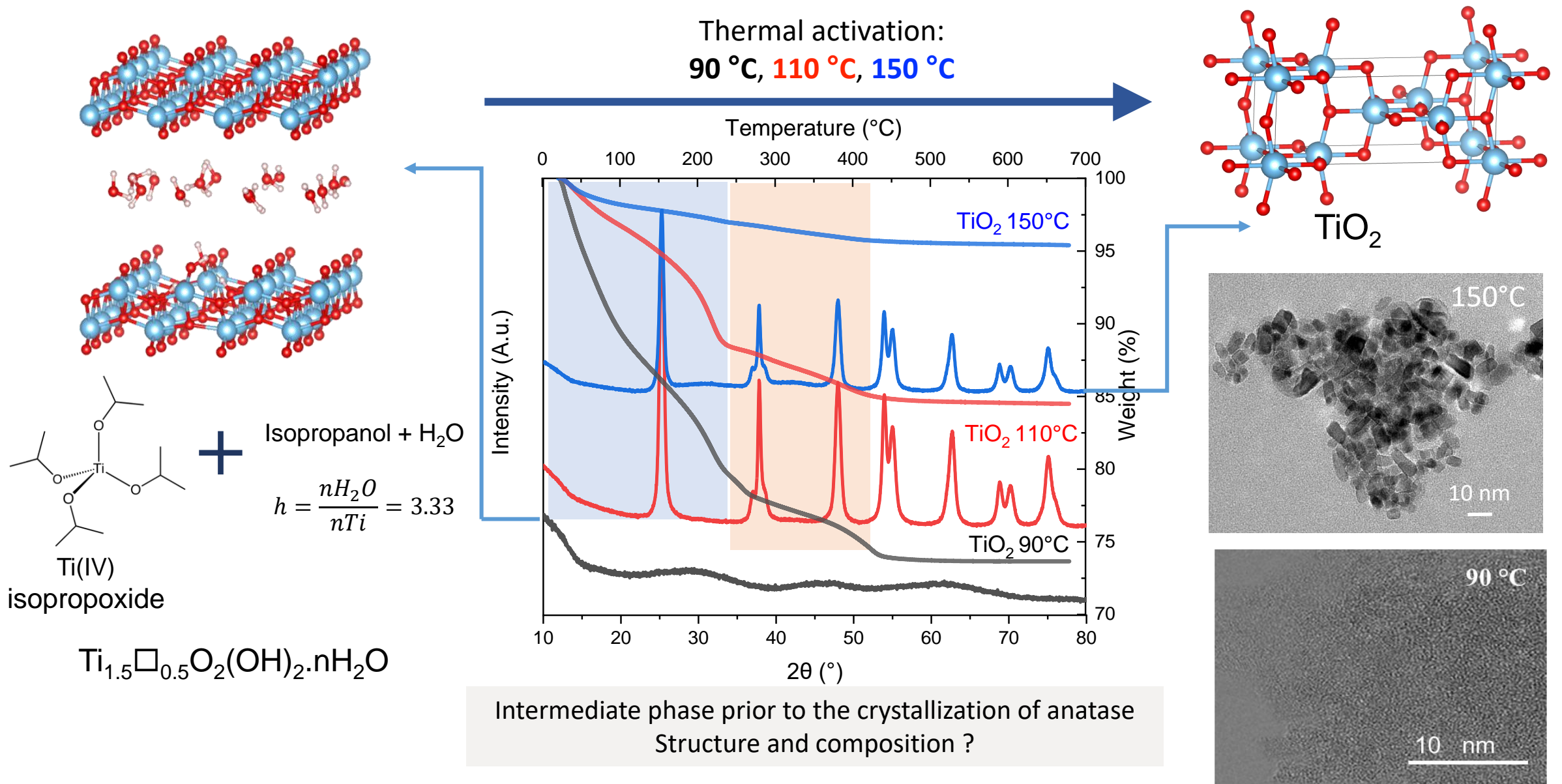
Controlling the structure of TiO₂ via the SOLVOTHERMAL approach



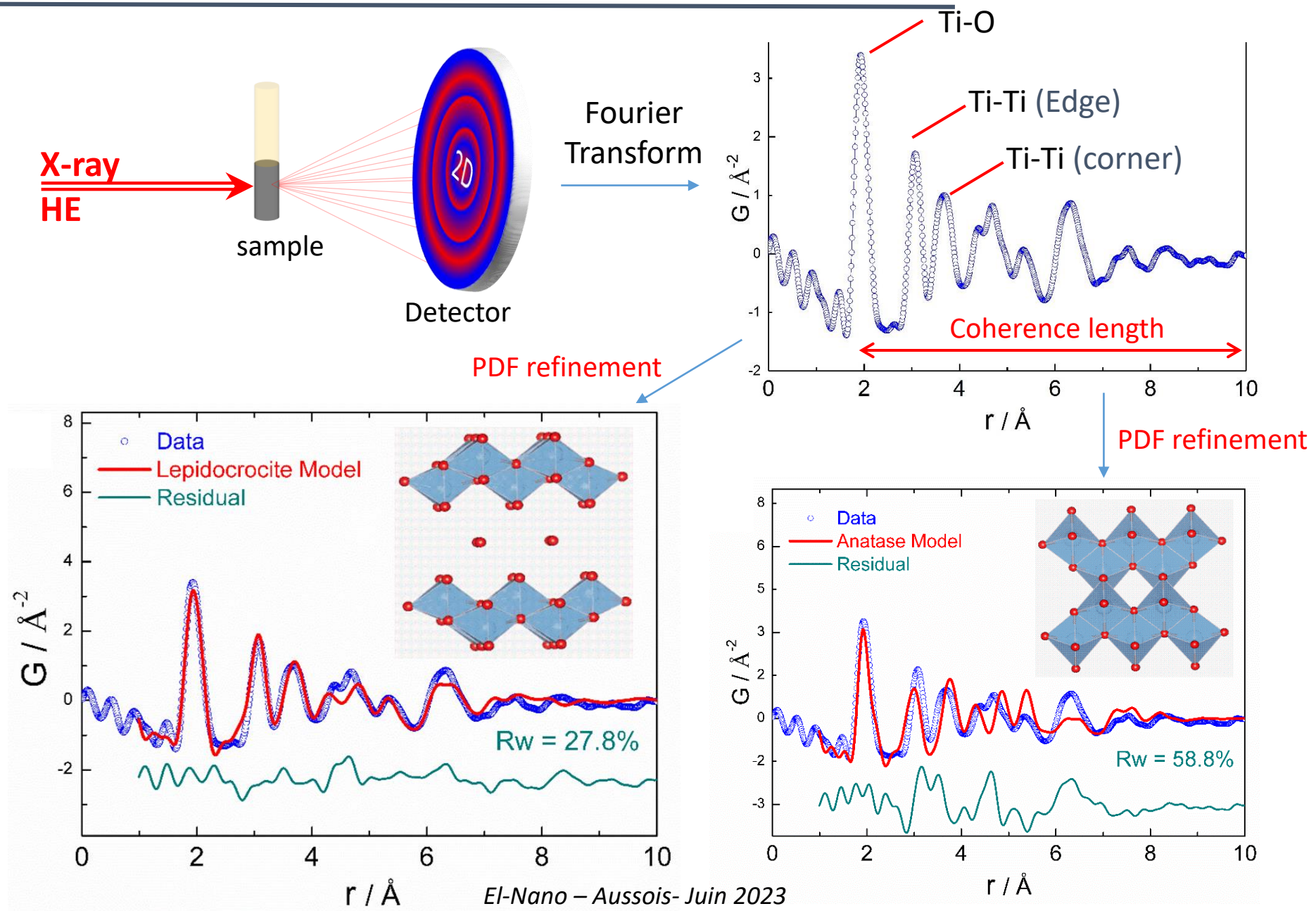
Controlling the structure of TiO₂ via the SOLVOTHERMAL approach



Controlling the structure of TiO₂ via the SOLVOTHERMAL approach

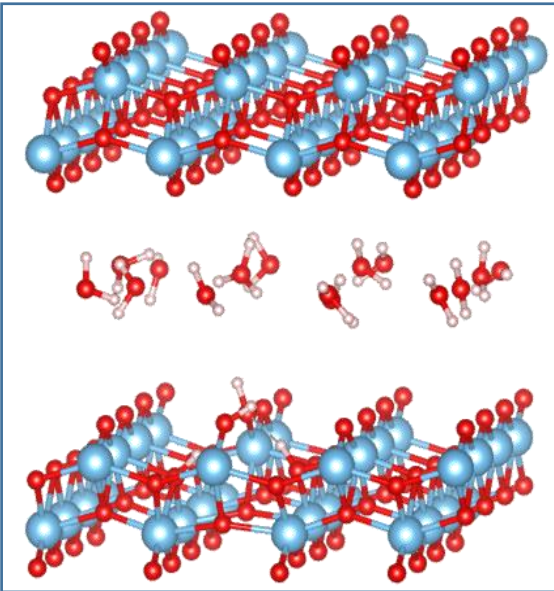


Controlling the structure of TiO_2 via the SOLVOTHERMAL approach

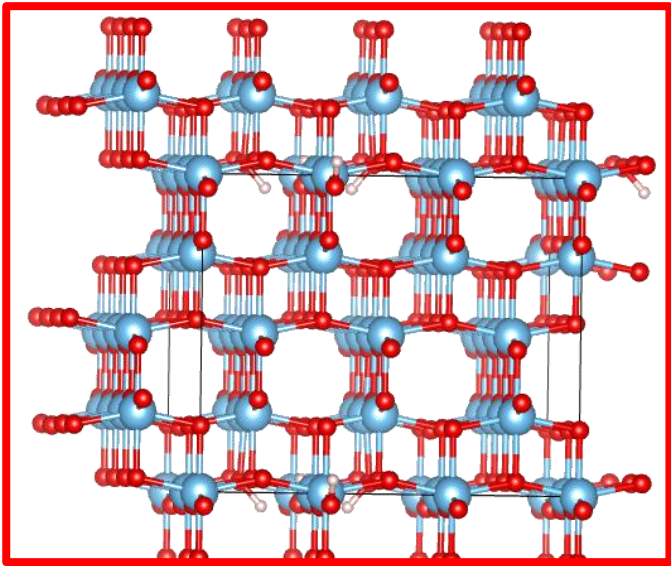


Controlling the structure of TiO₂ via the SOLVOTHERMAL approach : From amorphous to Crystal

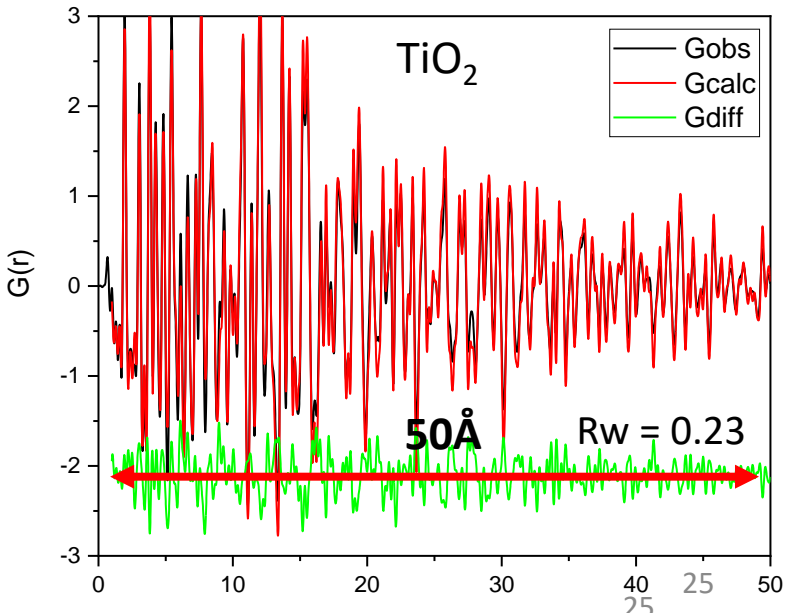
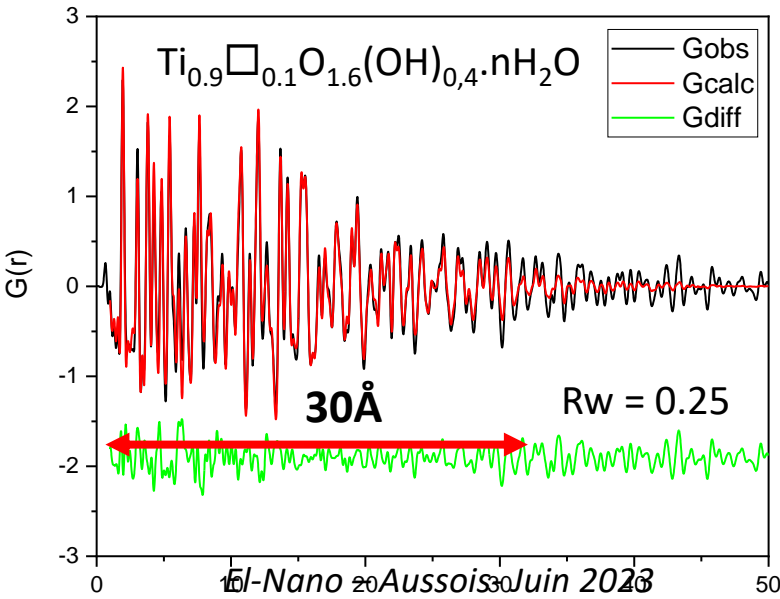
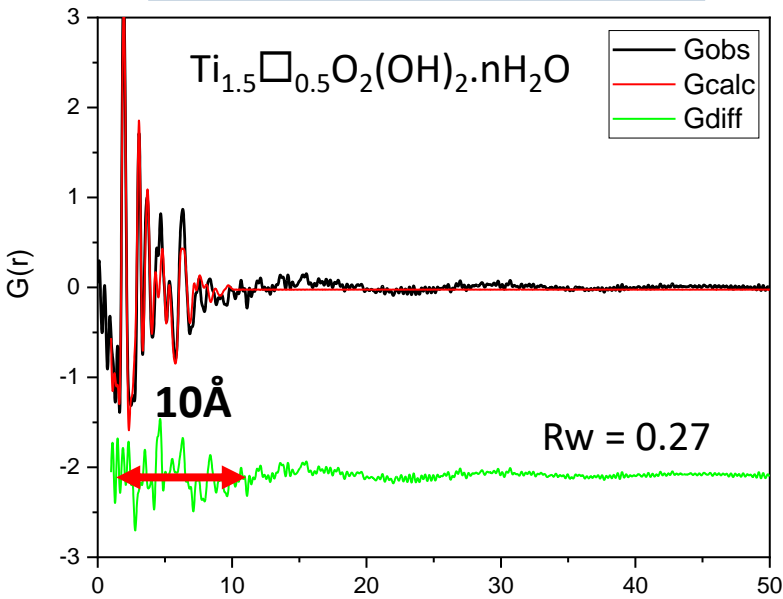
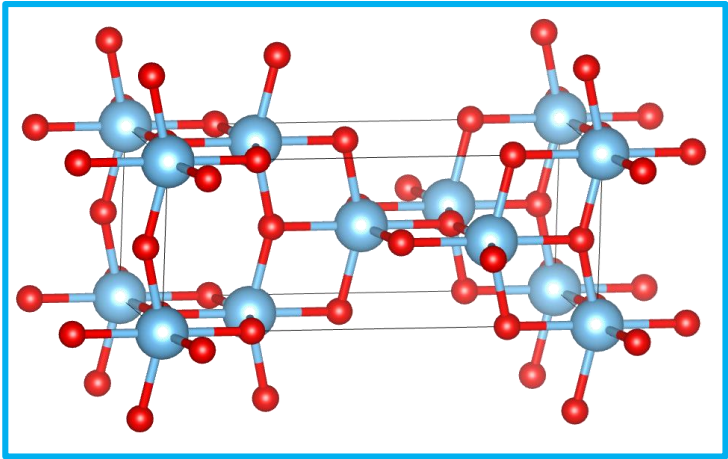
Lepidocrocite



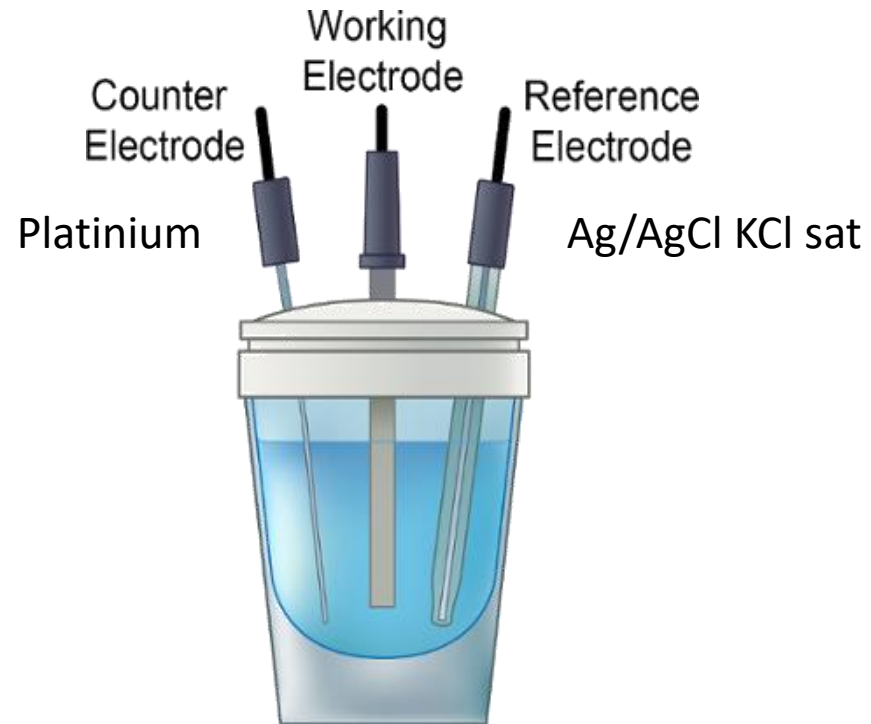
Defective Anatase



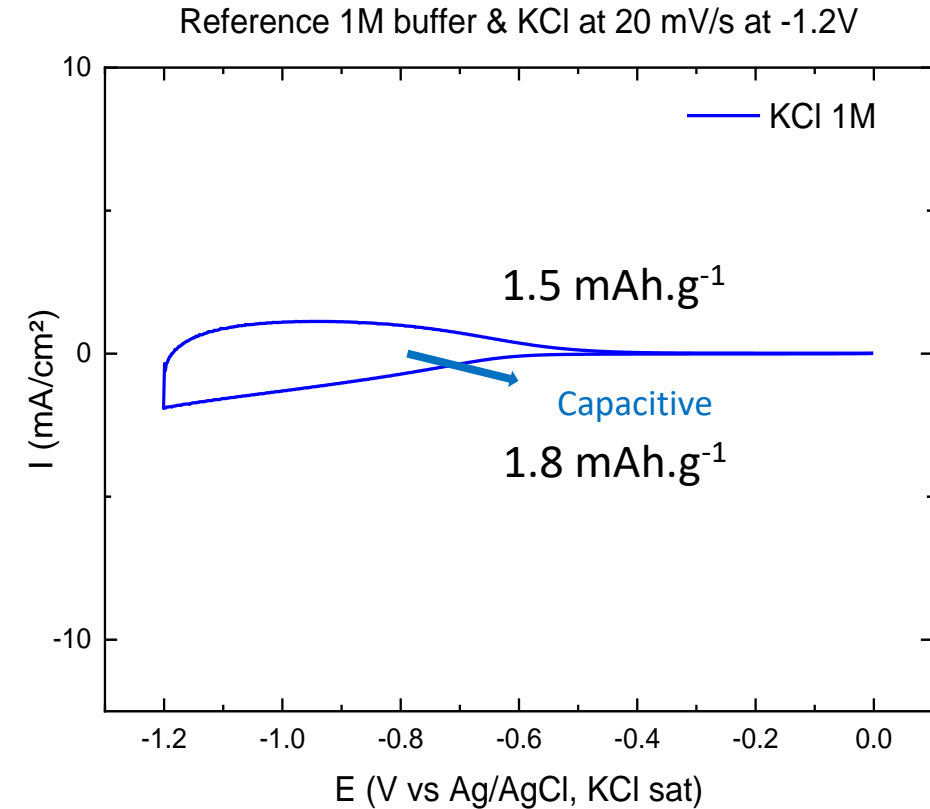
Pure Anatase



3 electrodes cells

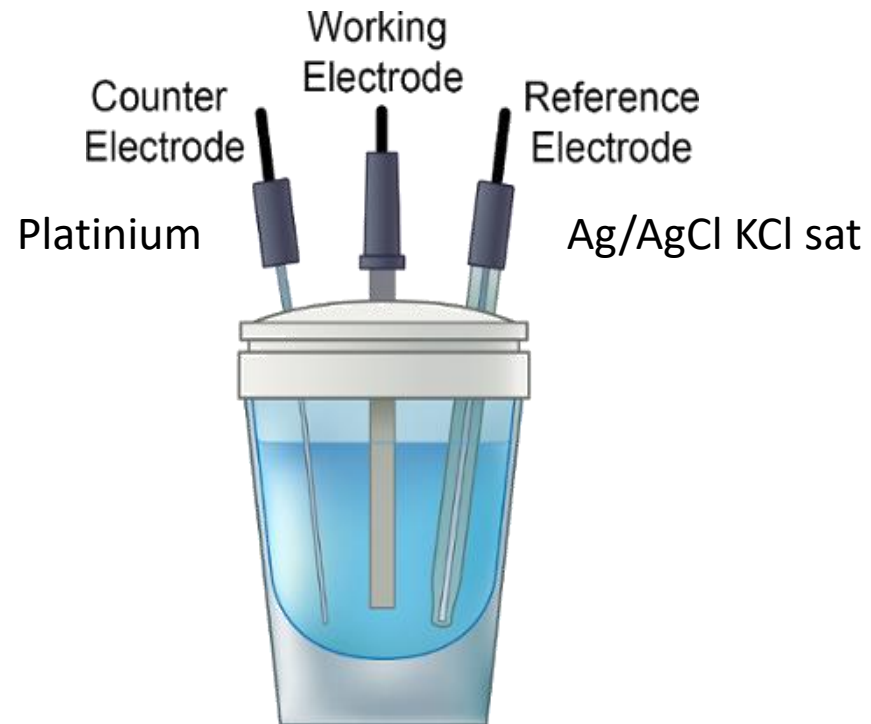


Ar bubling > 20 min

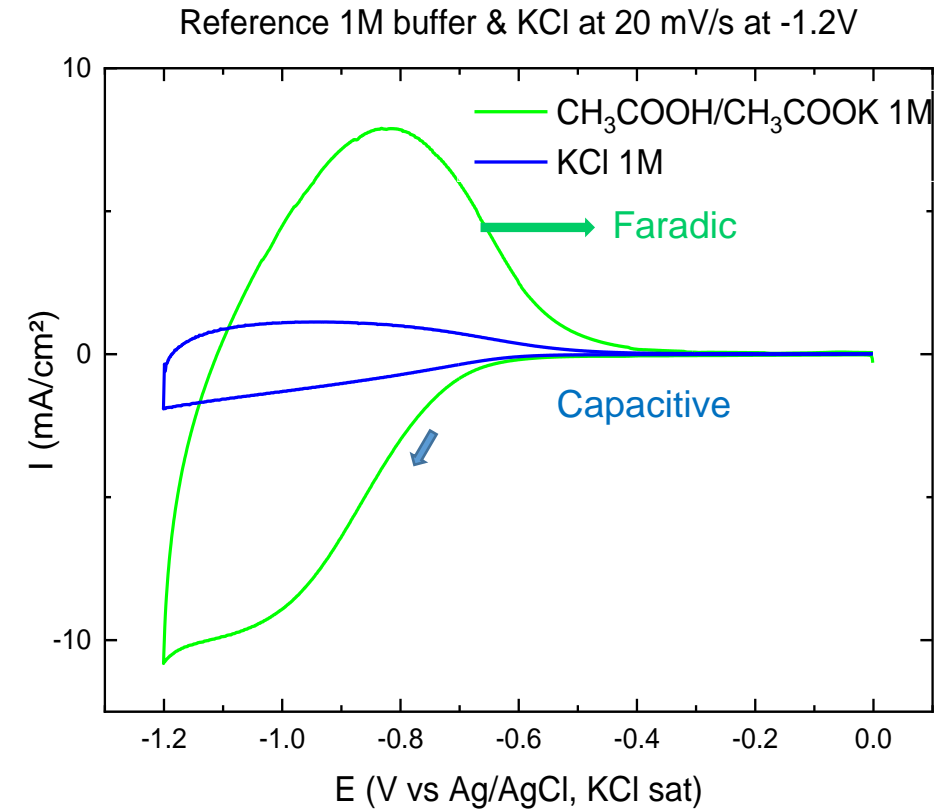


- KCl for **capacitive** contribution (adsorption/desorption of K^+)

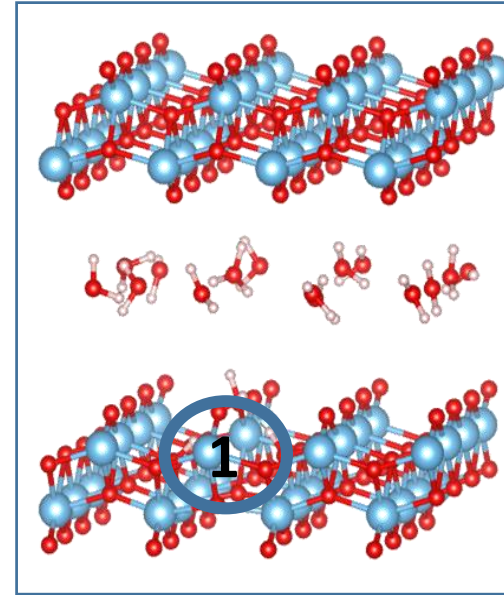
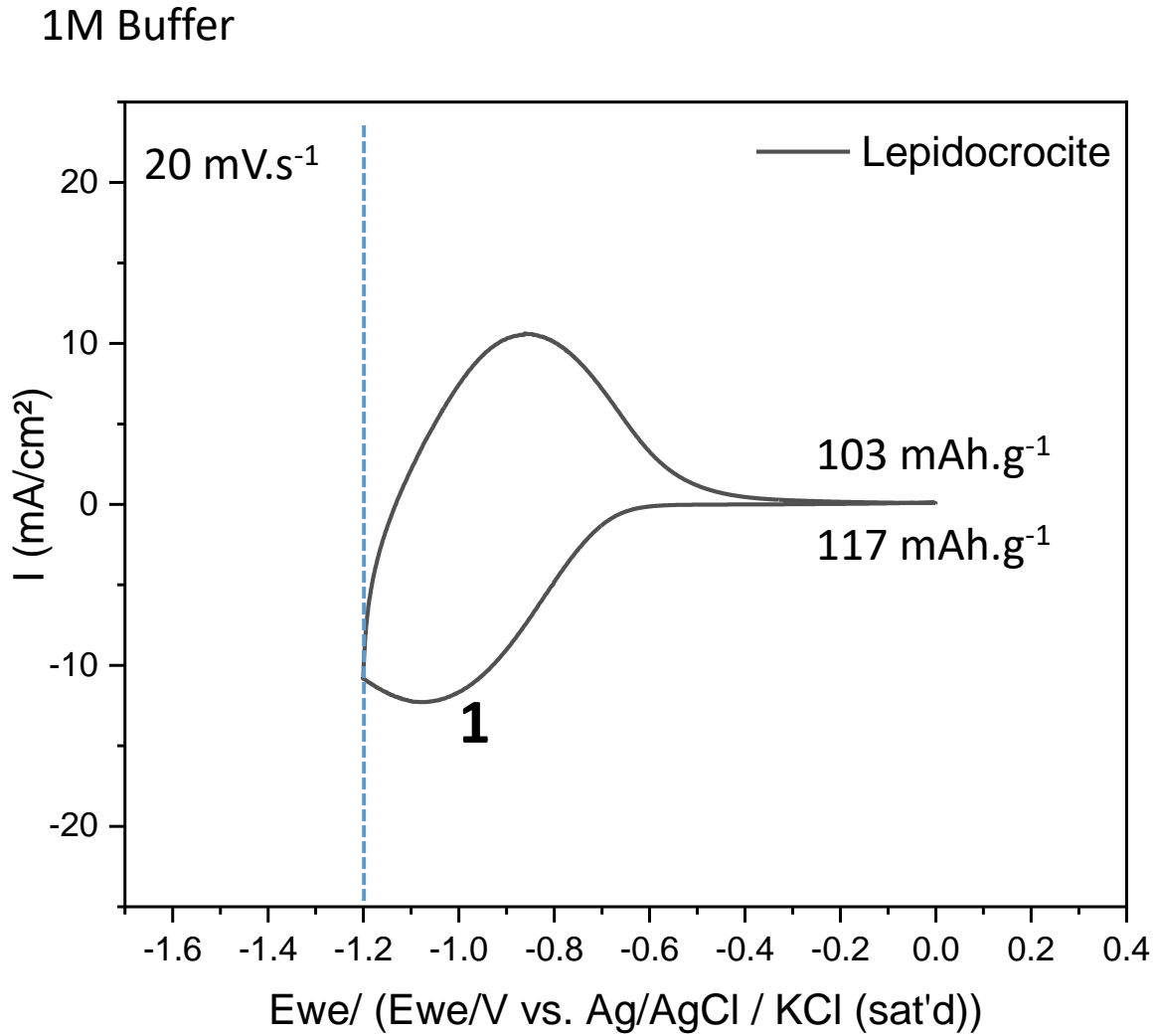
3 electrodes cells



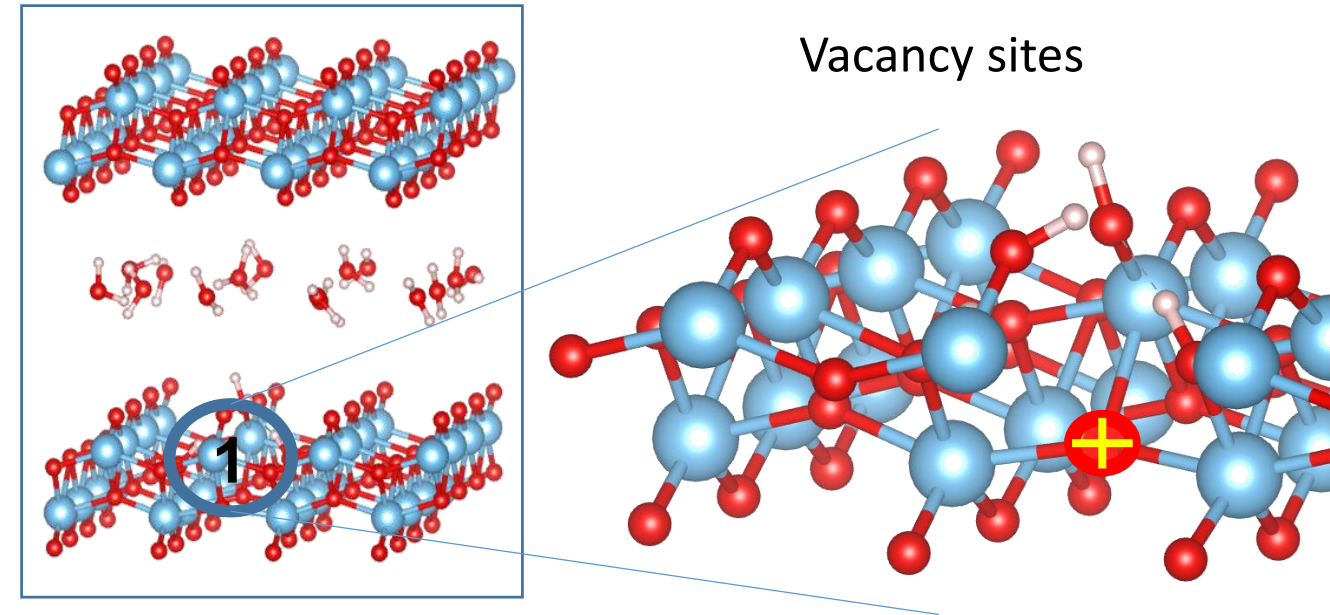
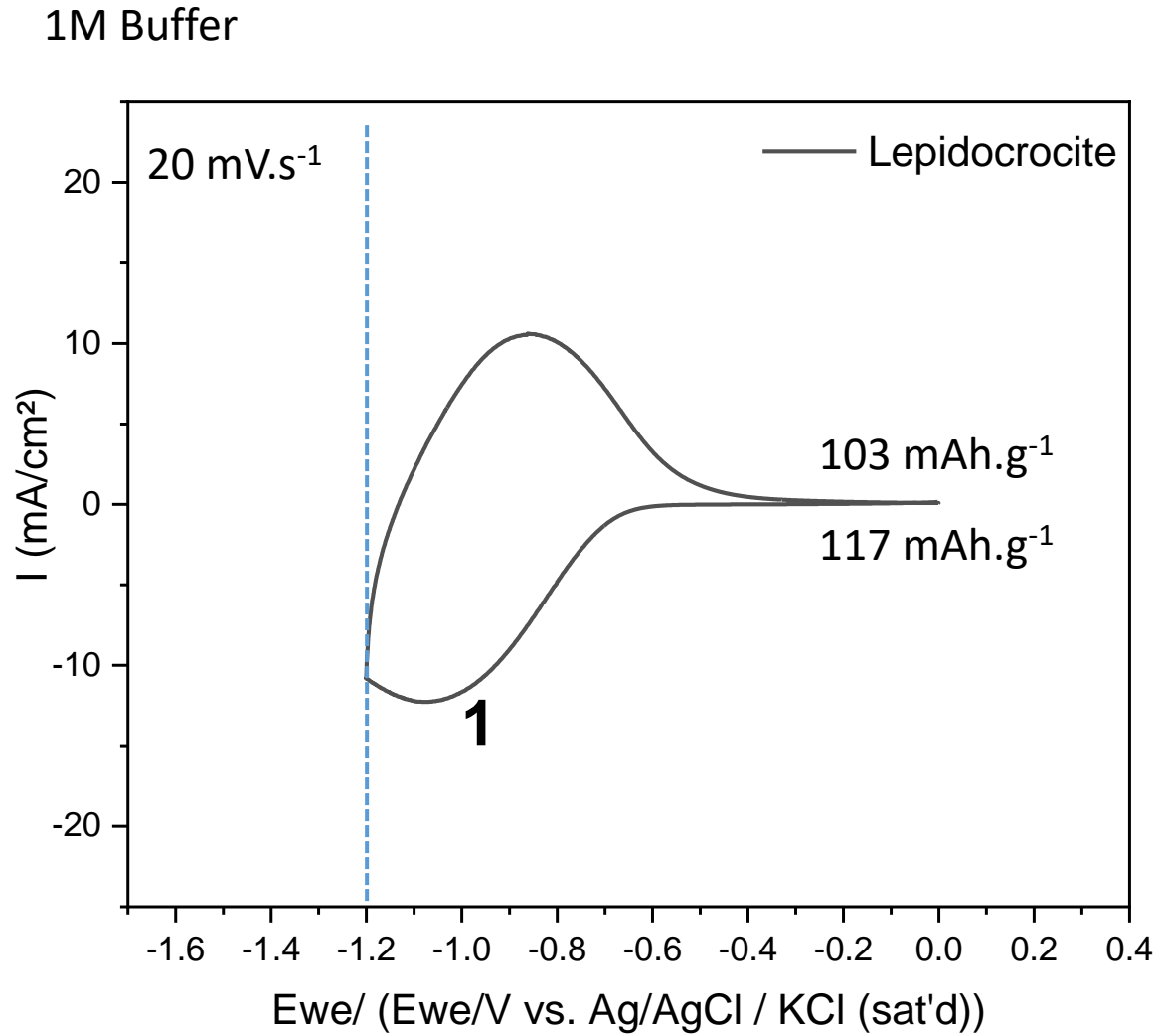
Ar bubling > 20 min



- KCl for **capacitive** contribution (adsorption/desorption of K^+)
- Buffer pH=5 for **faradic** contribution (intercalation/de-intercalation of H^+)

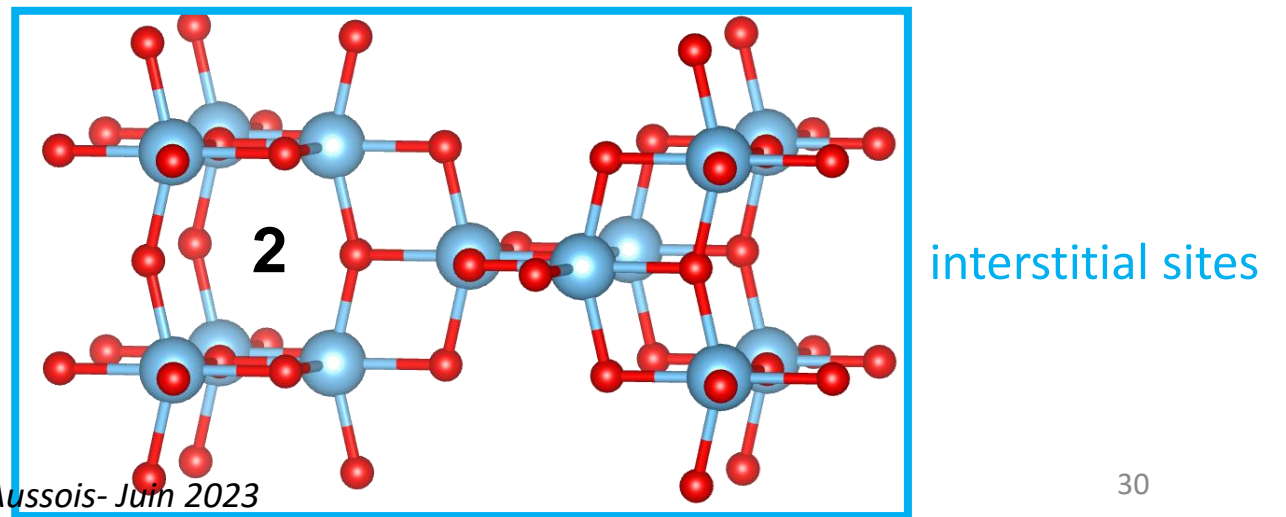
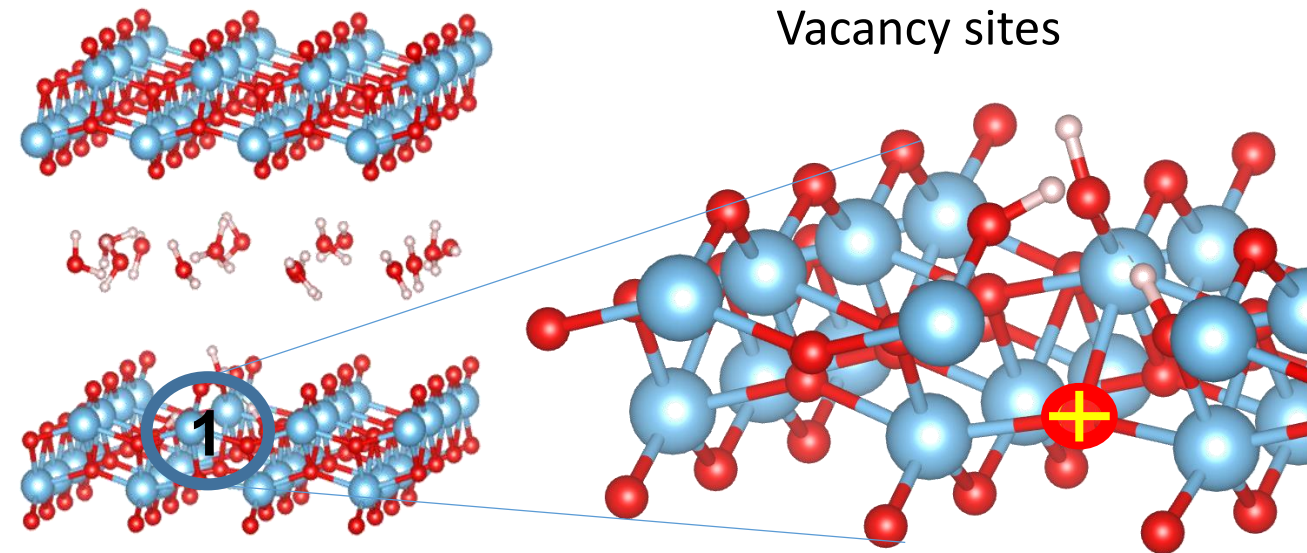
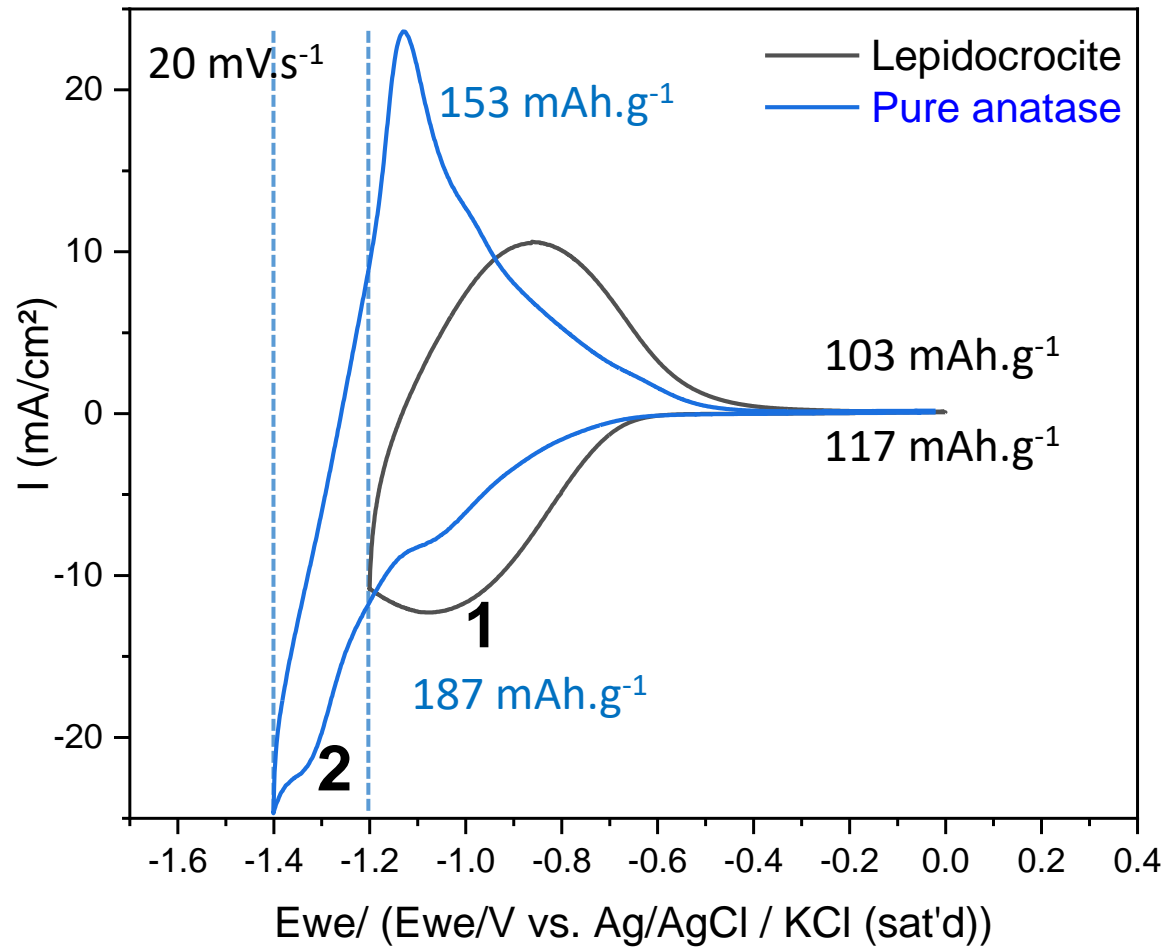


Vacancy sites



Impact of the TiO₂ Structure onto Electrochemistry

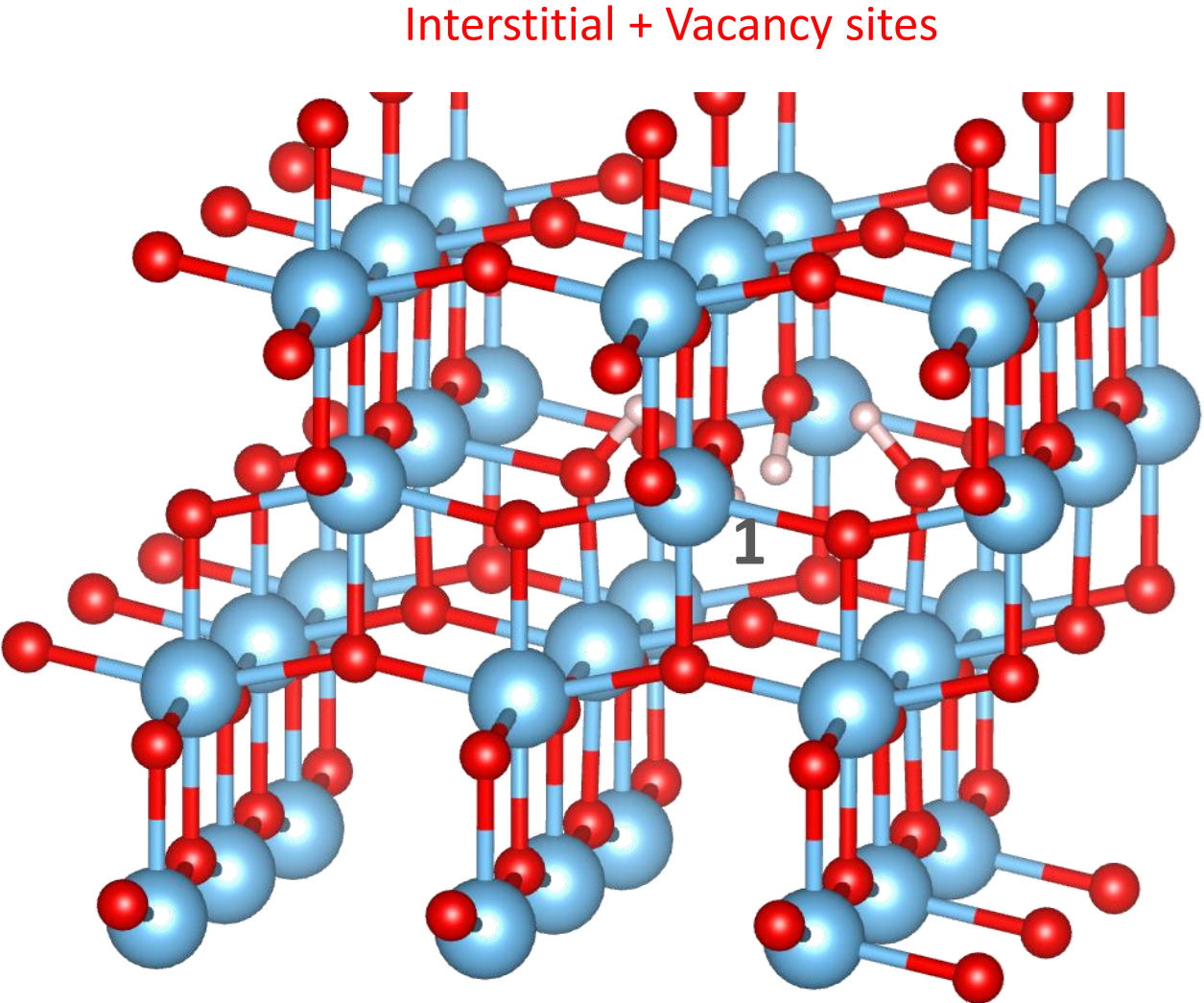
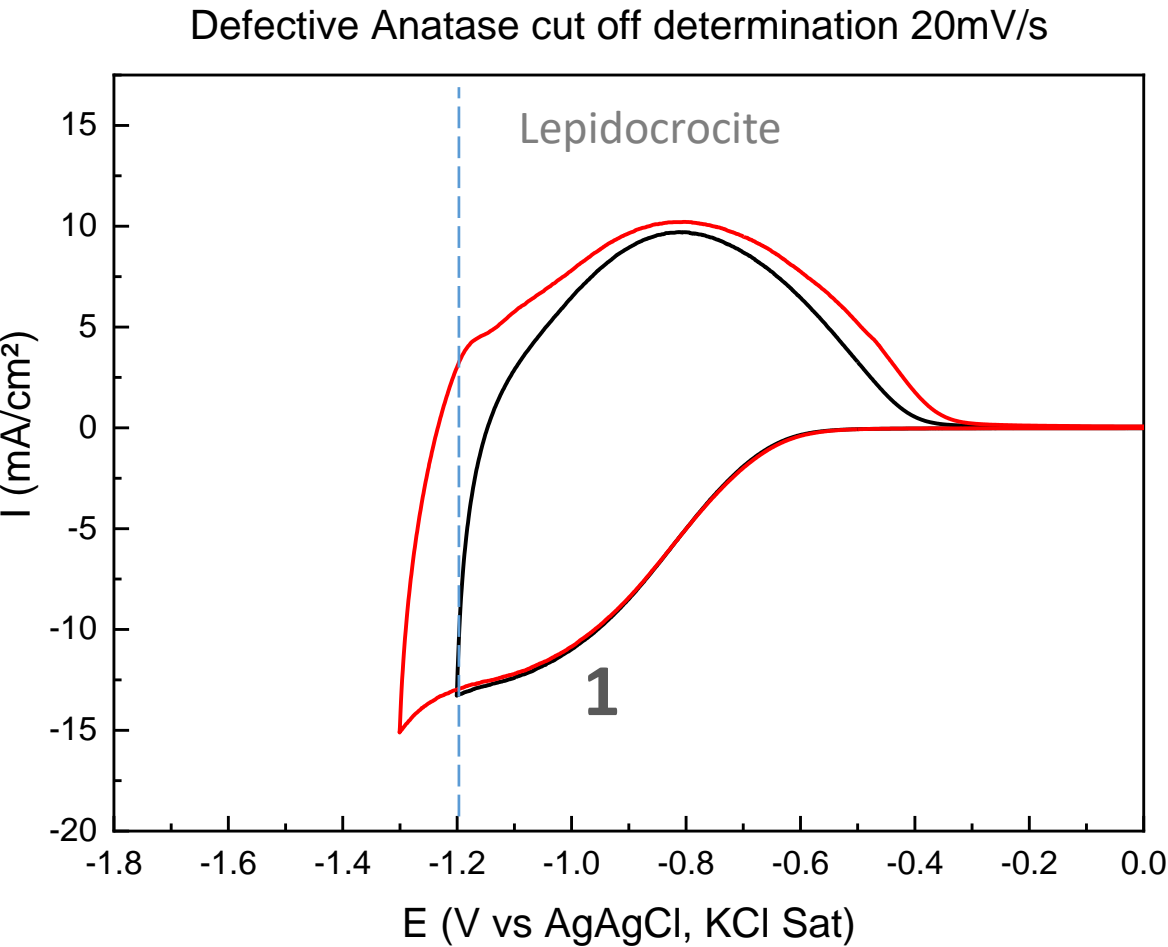
1M Buffer



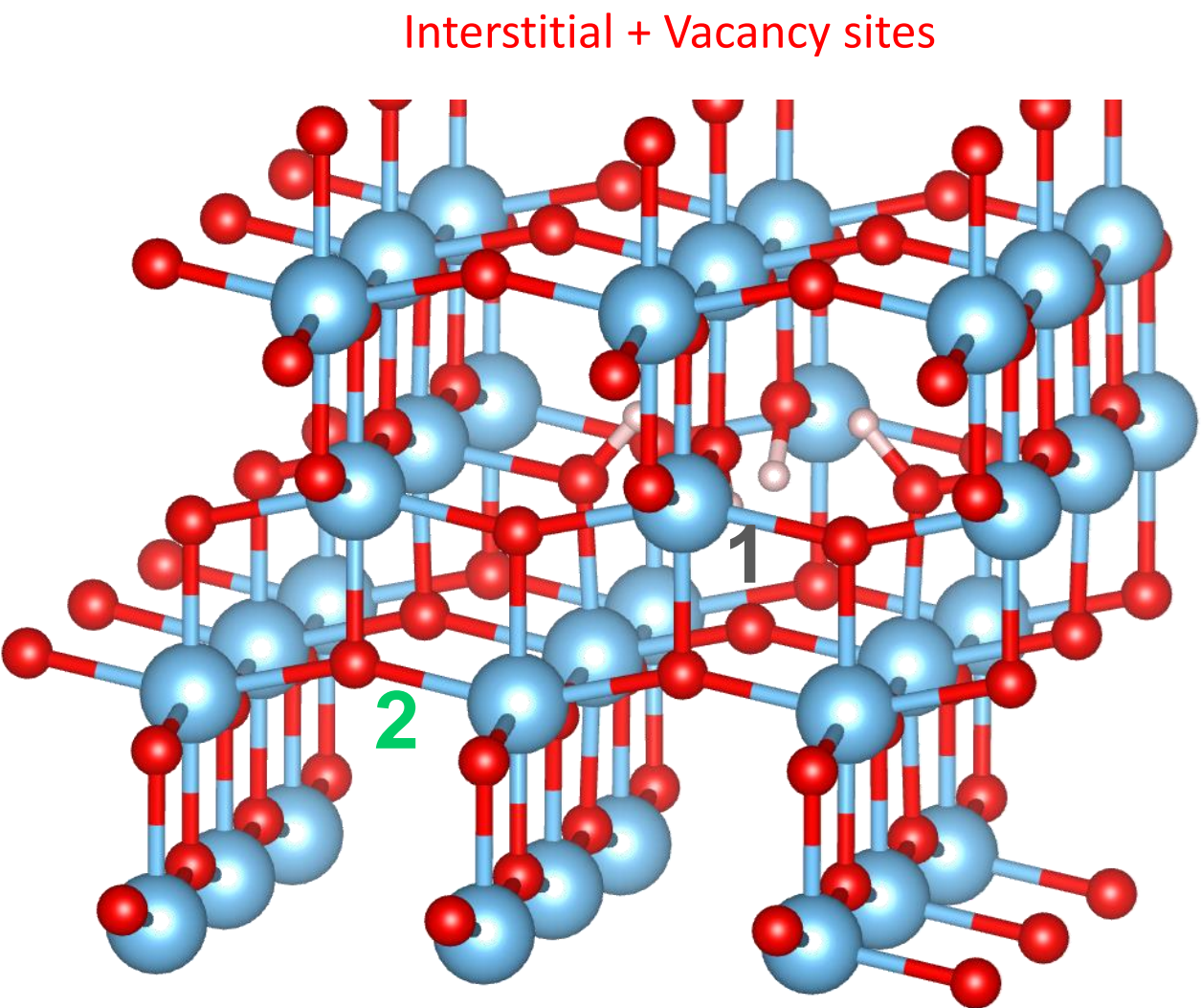
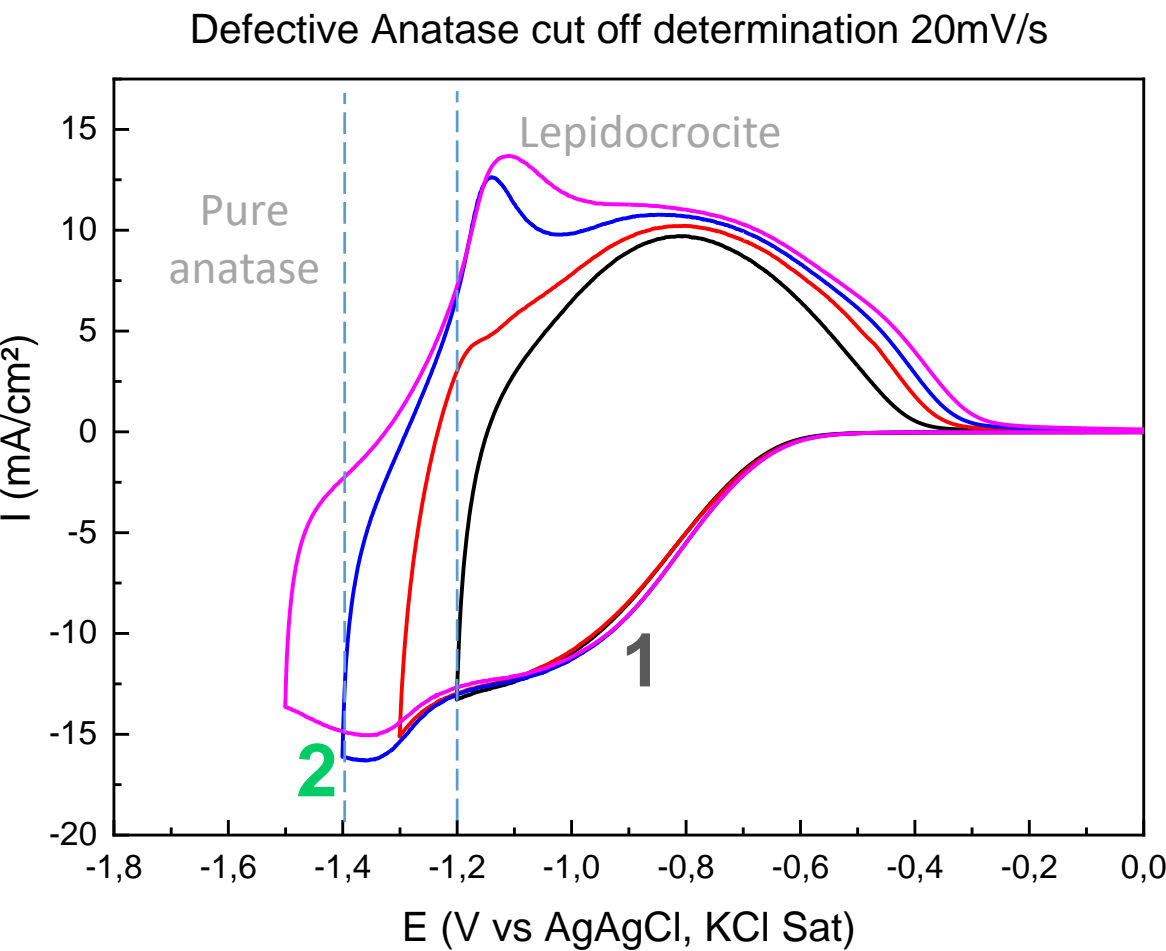
(1) $E_{\text{intercalation}}(\text{H}^+)$ in anatase = -1.215 V vs Ag/AgCl, KCl sat

(2) Makivić, N.; Evidence of Bulk Proton Insertion in Nanostructured Anatase and Amorphous TiO₂ Electrodes. *Chem. Mater.* **2021**, 33 (9), 3436–3448.

1M Buffer

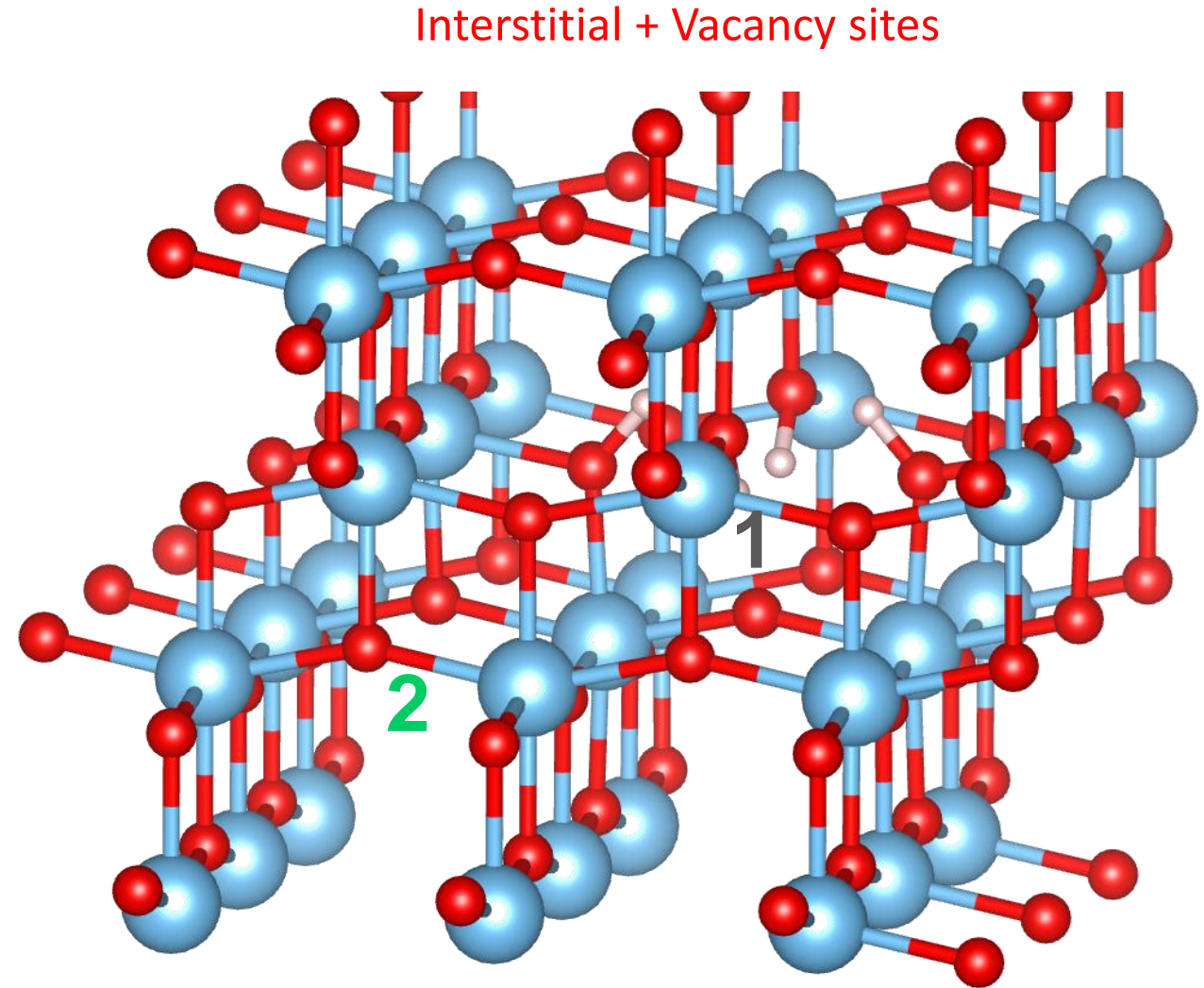
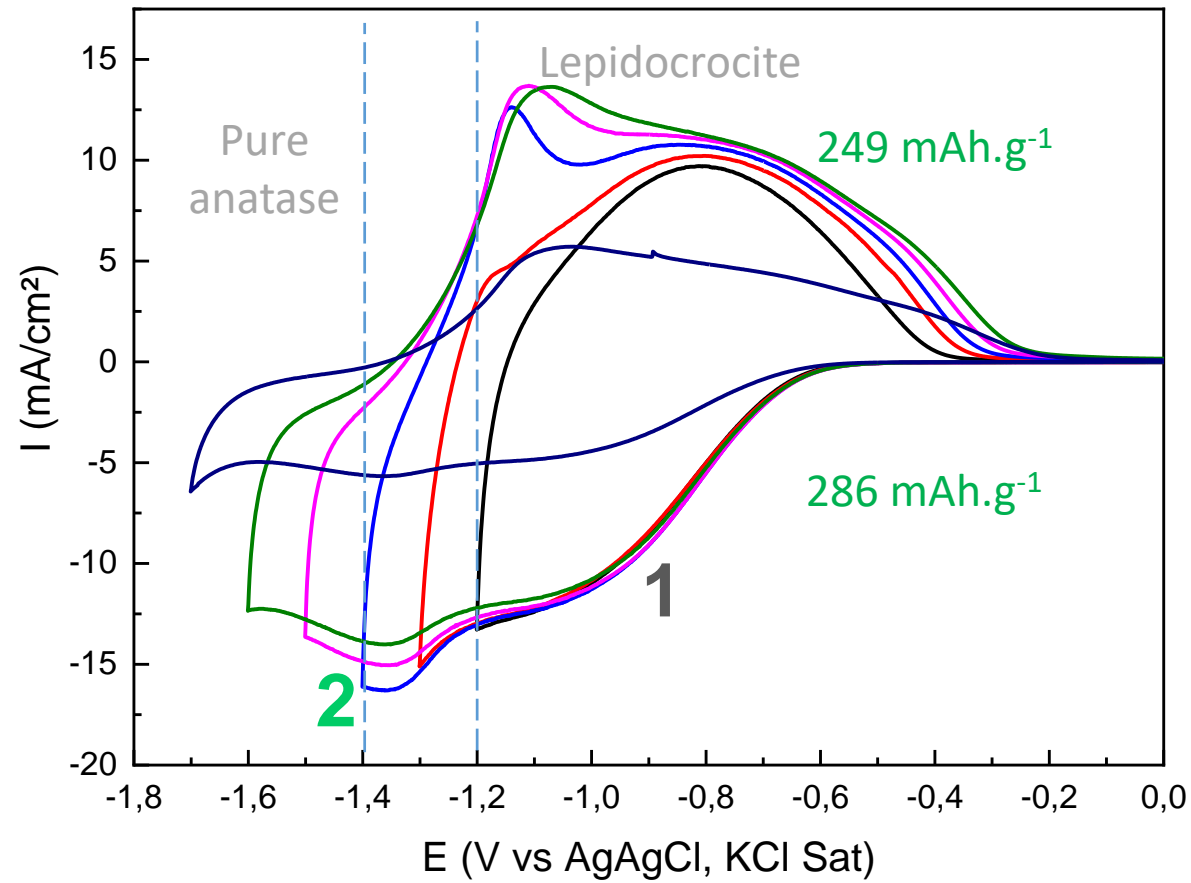


1M Buffer



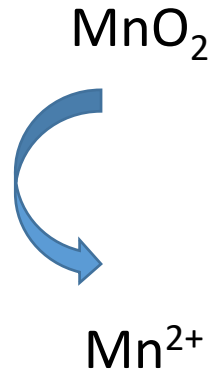
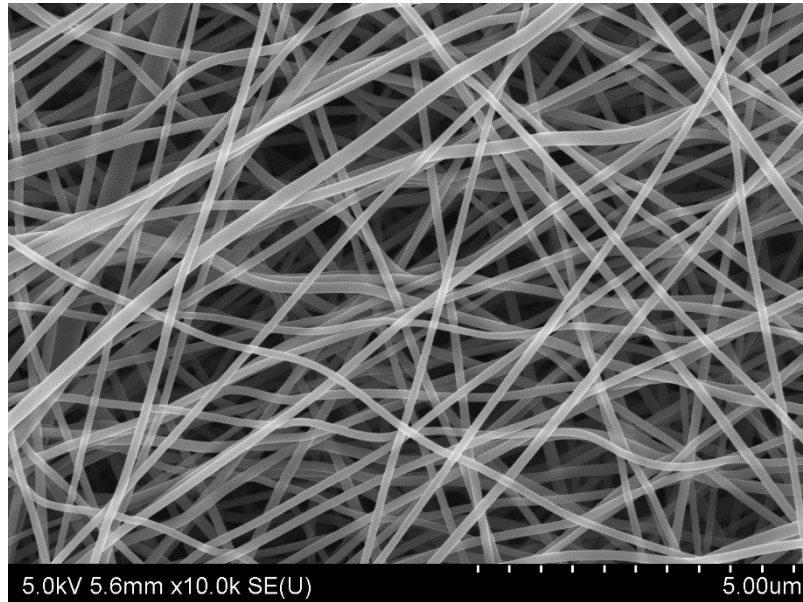
1M Buffer

Defective Anatase cut off determination 20mV/s

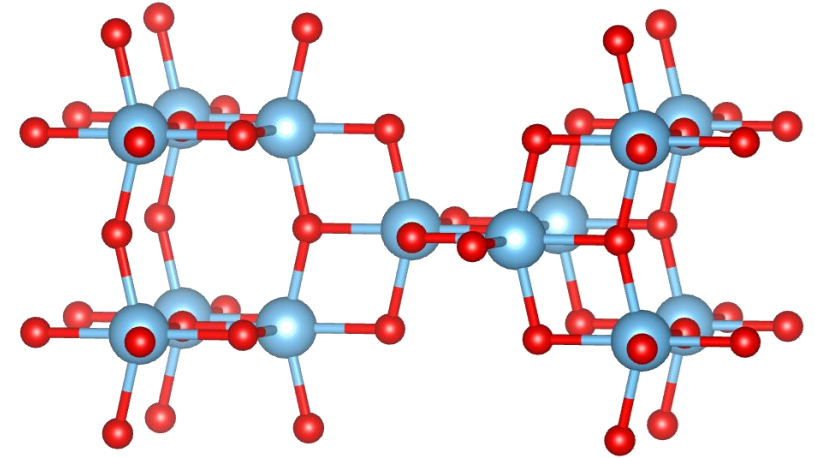




Electrospun - CNF



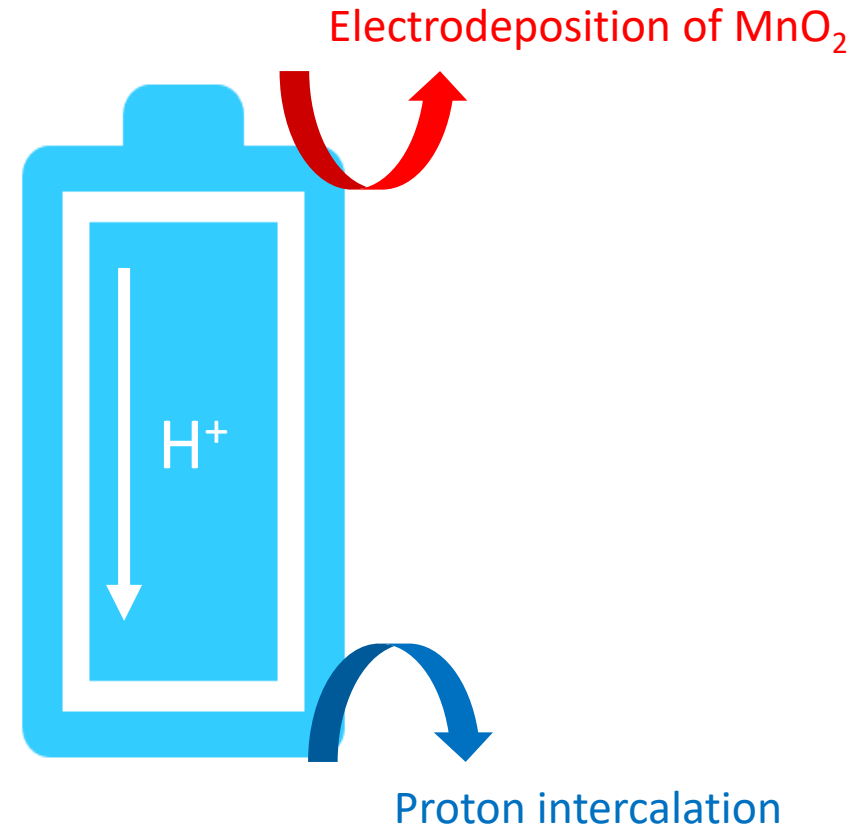
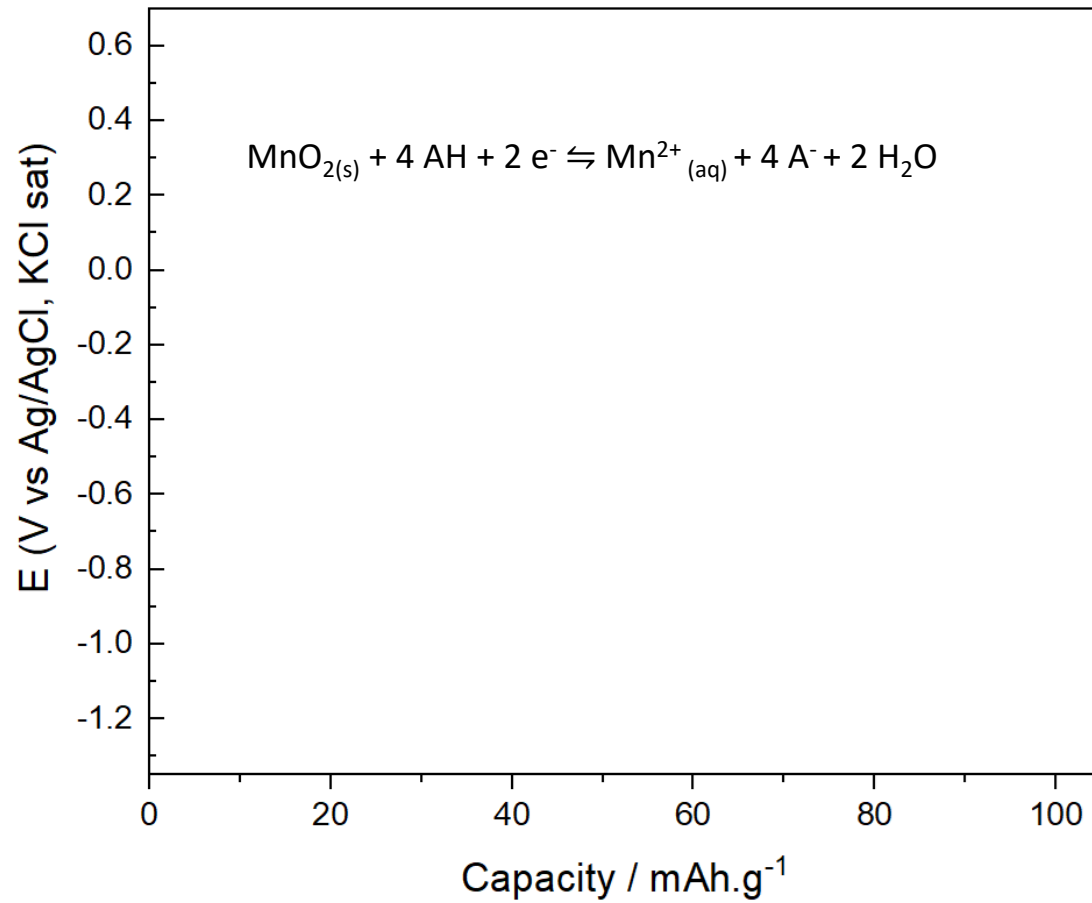
Titanate materials



Design a **safe, eco-friendly**, and **low-cost** battery for energy **buffer** application

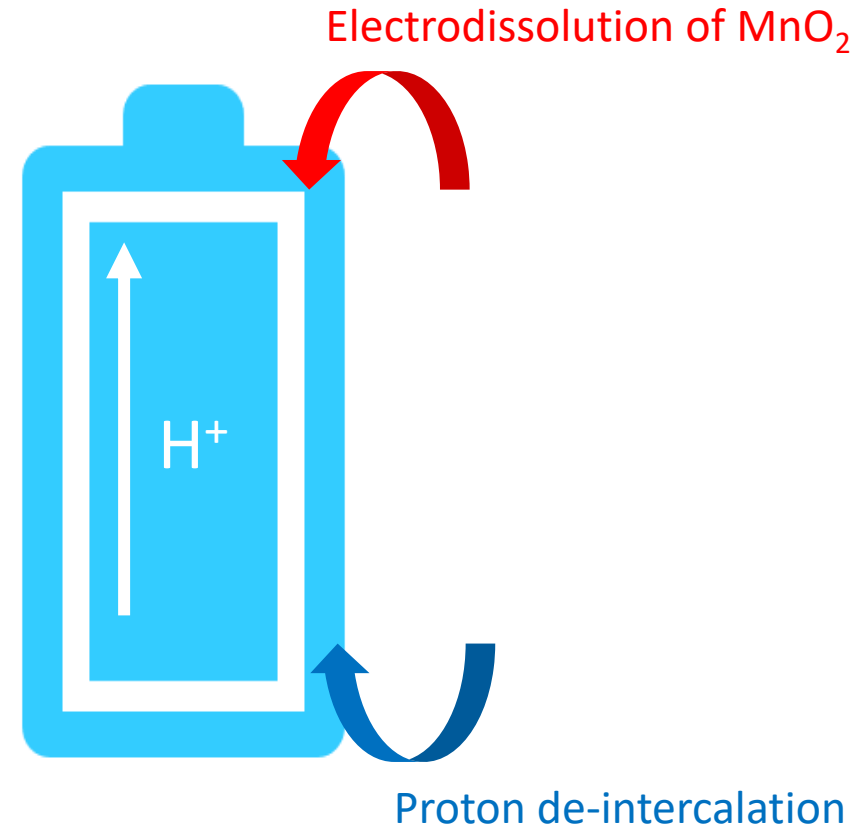
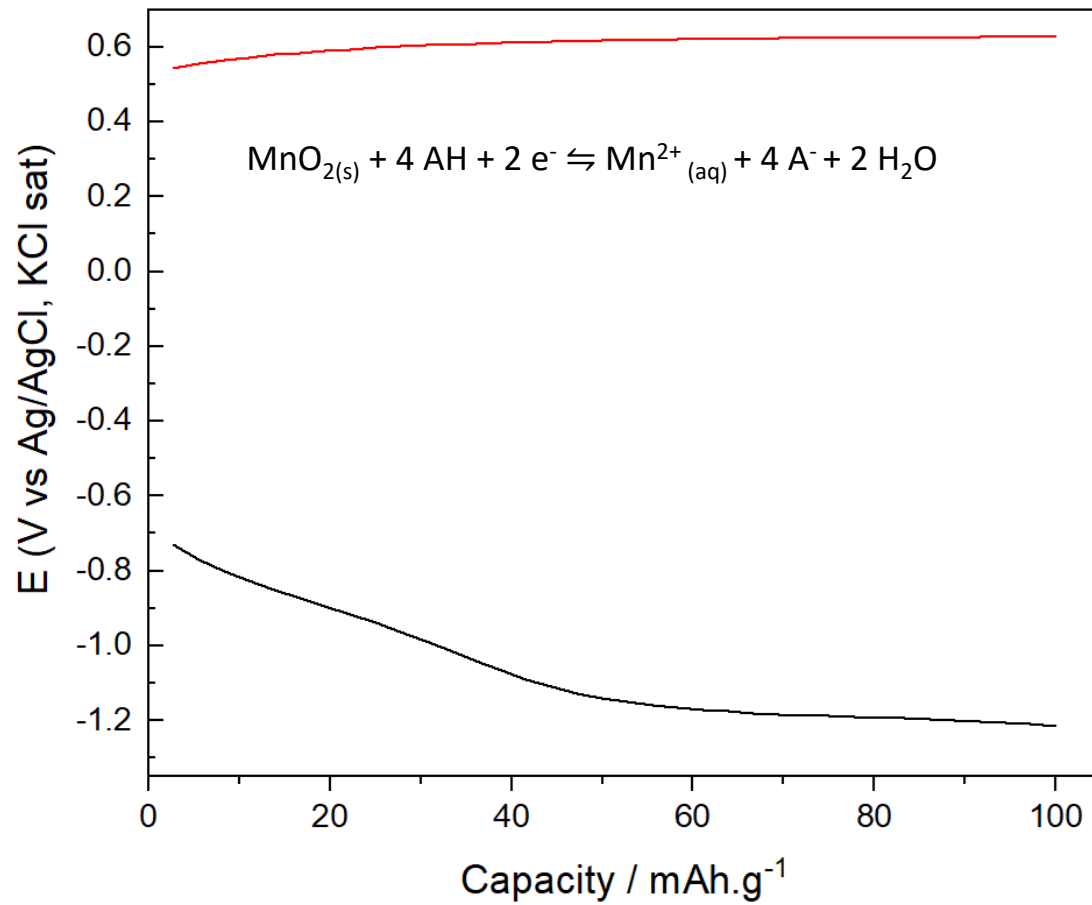
$$\Delta E = 1.4 \sim 1.8 \text{ V}$$

$$10 \text{ A.g}^{-1}$$



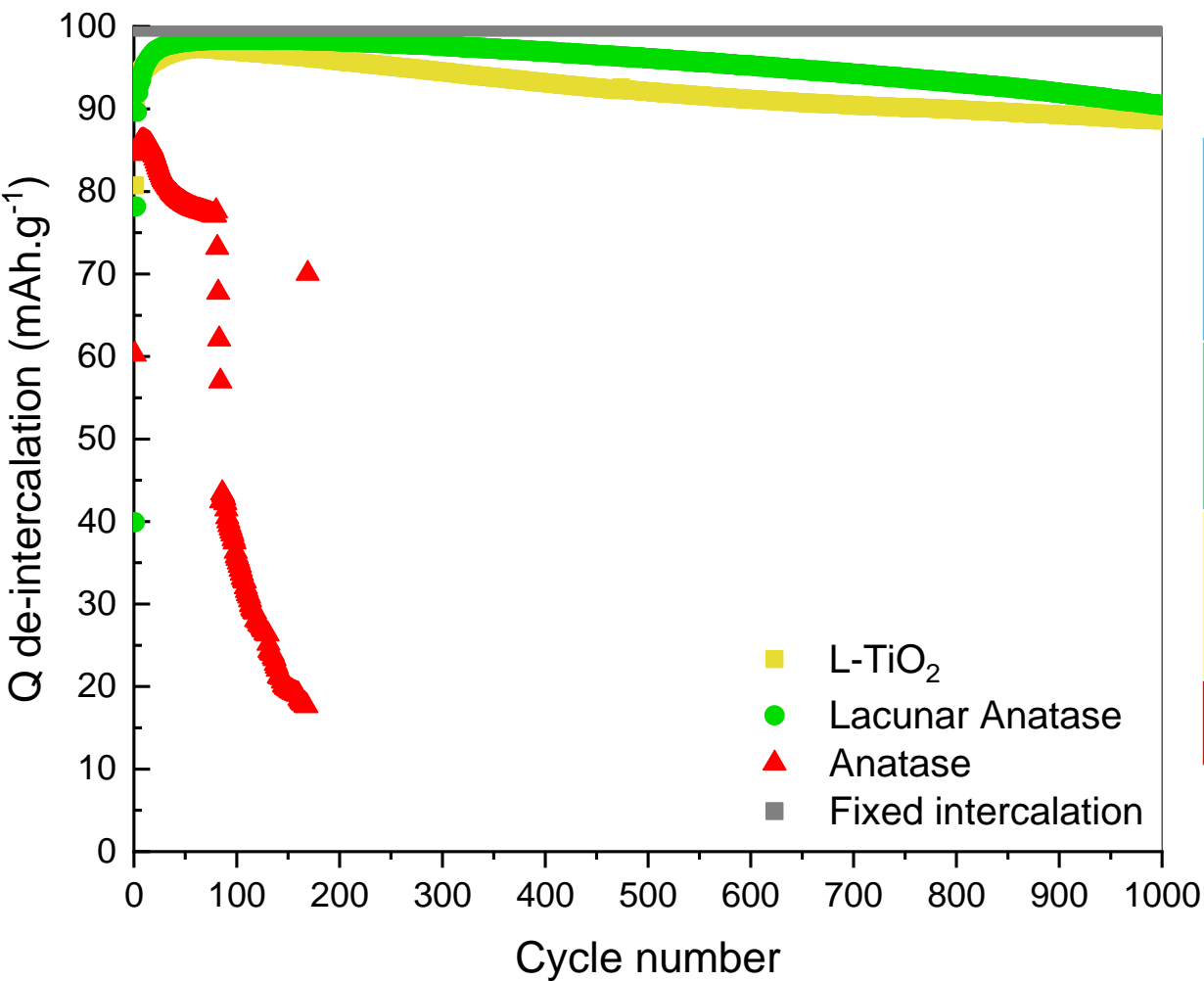
$$\Delta E = 1.4 \sim 1.8 \text{ V}$$

$$10 \text{ A.g}^{-1}$$



Full Cell battery : MnO₂ vs. TiO₂

10 A.g⁻¹ Mild accumulation conditions



Materials	Energy [Wh/Kg]	Ece-Ewe [V]	Cyclability	CE [%]
Defective Anatase	105	1.4~1.8	>1000	95
L-TiO ₂	90	1.4~1.6	>1000	92
Anatase	62	1.6~1.8	<100	75

Chemistry of Nanomaterials : a fundamental bottleneck& one possible solution

SOFT & GREEN CHEMISTRY

100°C

300°C

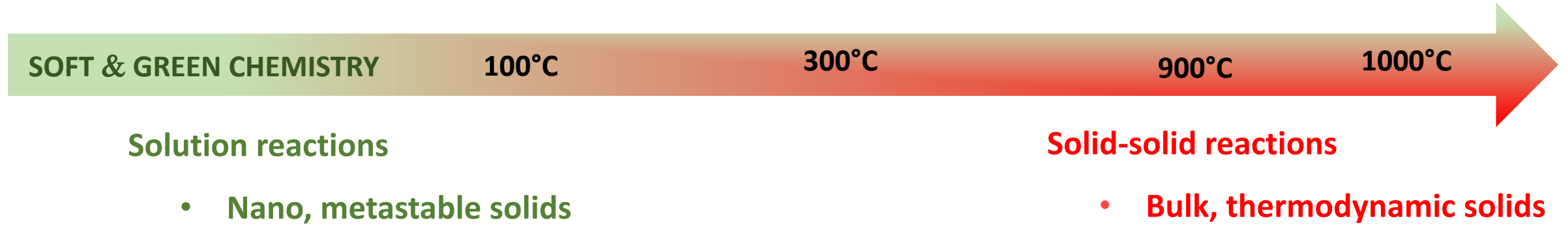
900°C

1000°C

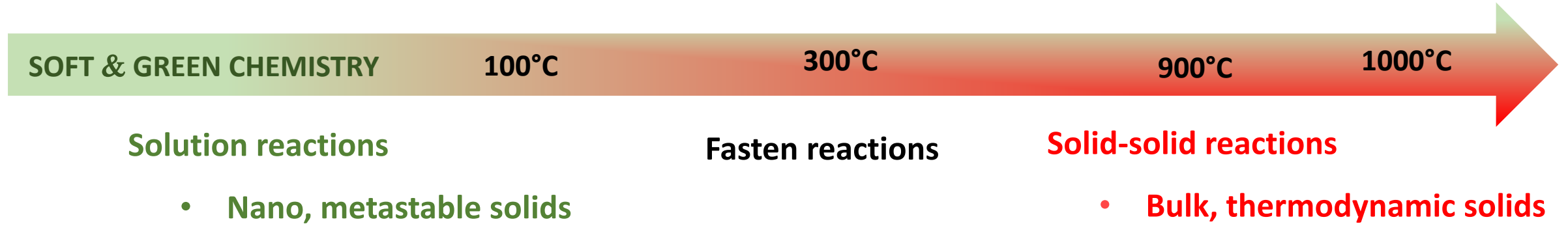
Solution reactions

- **Nano, metastable solids**

Chemistry of Nanomaterials : a fundamental bottleneck& one possible solution



Chemistry of Nanomaterials : a fundamental bottleneck& one possible solution



Chemistry of Nanomaterials : a fundamental bottleneck& one possible solution

SOFT & GREEN CHEMISTRY

100°C

300°C

900°C

1000°C

Solution reactions

- **Nano, metastable solids**

Fasten reactions

Solid-solid reactions

- **Bulk, thermodynamic solids**

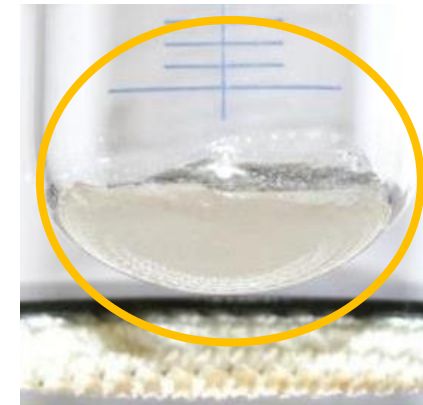
High temperature liquids?



Molten Salt Synthesis



Eutectic LiCl-KCl
melting 353°C



- ✓ Viscosity ~ water
- ✓ Stability ~ 900°C
- ✓ Negligible vapor pressure

Chemistry of Nanomaterials : a fundamental bottleneck& one possible solution



Solution reactions

- Nano, metastable solids

Fasten reactions

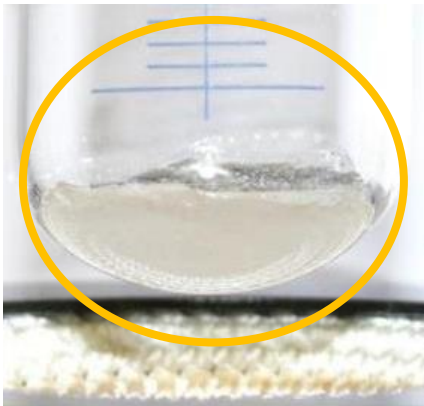
Solid-solid reactions

- Bulk, thermodynamic solids

High temperature liquids?

Eutectic LiCl-KCl
melting 353°C

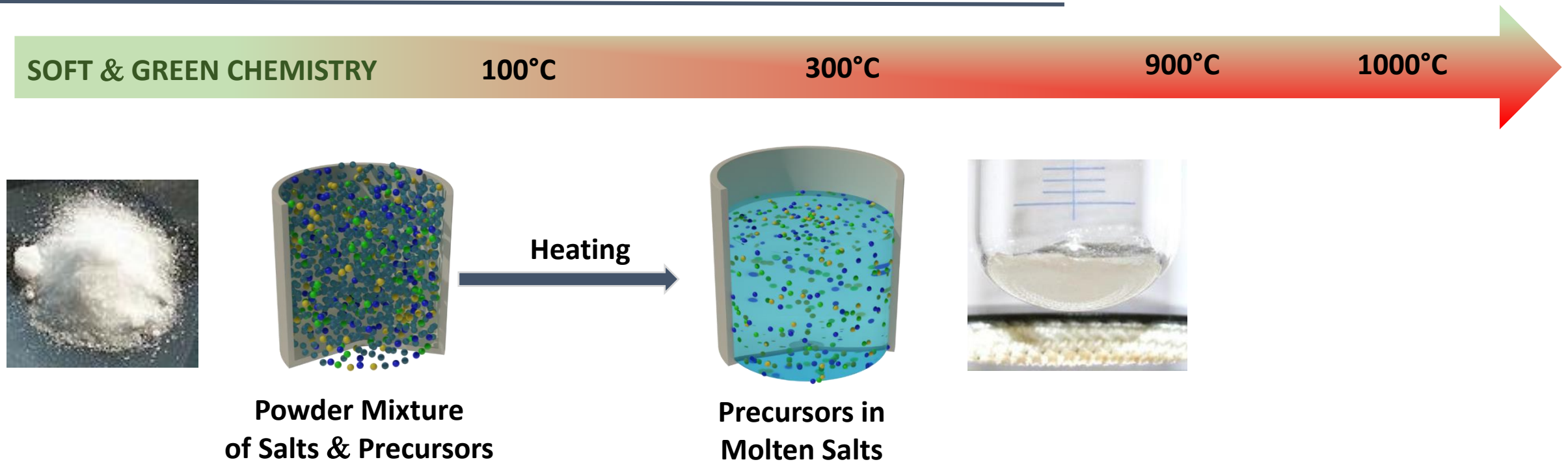
Molten Salt Synthesis

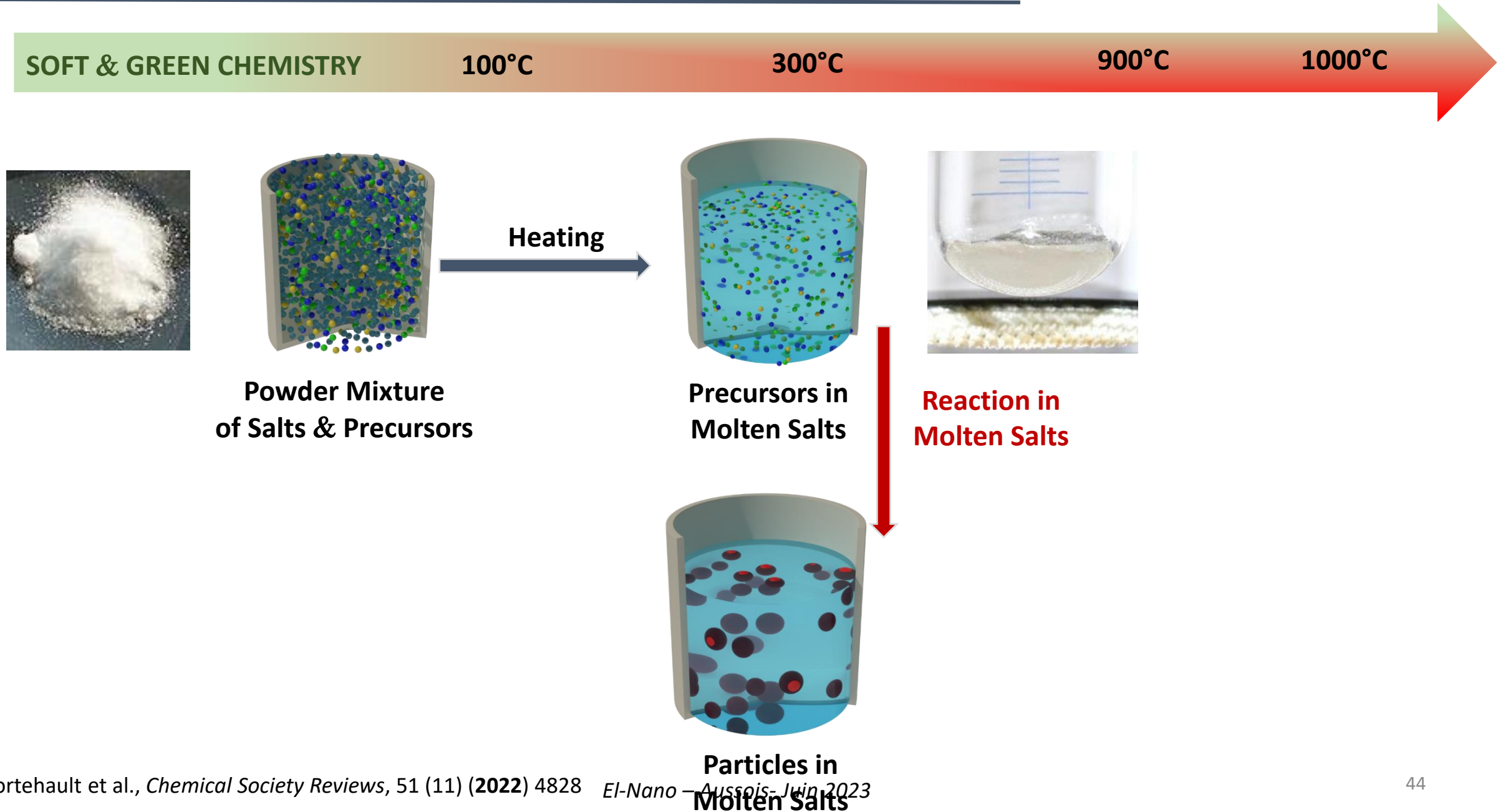


Evaporites Minerals : halides, carbonates, sulfates,...

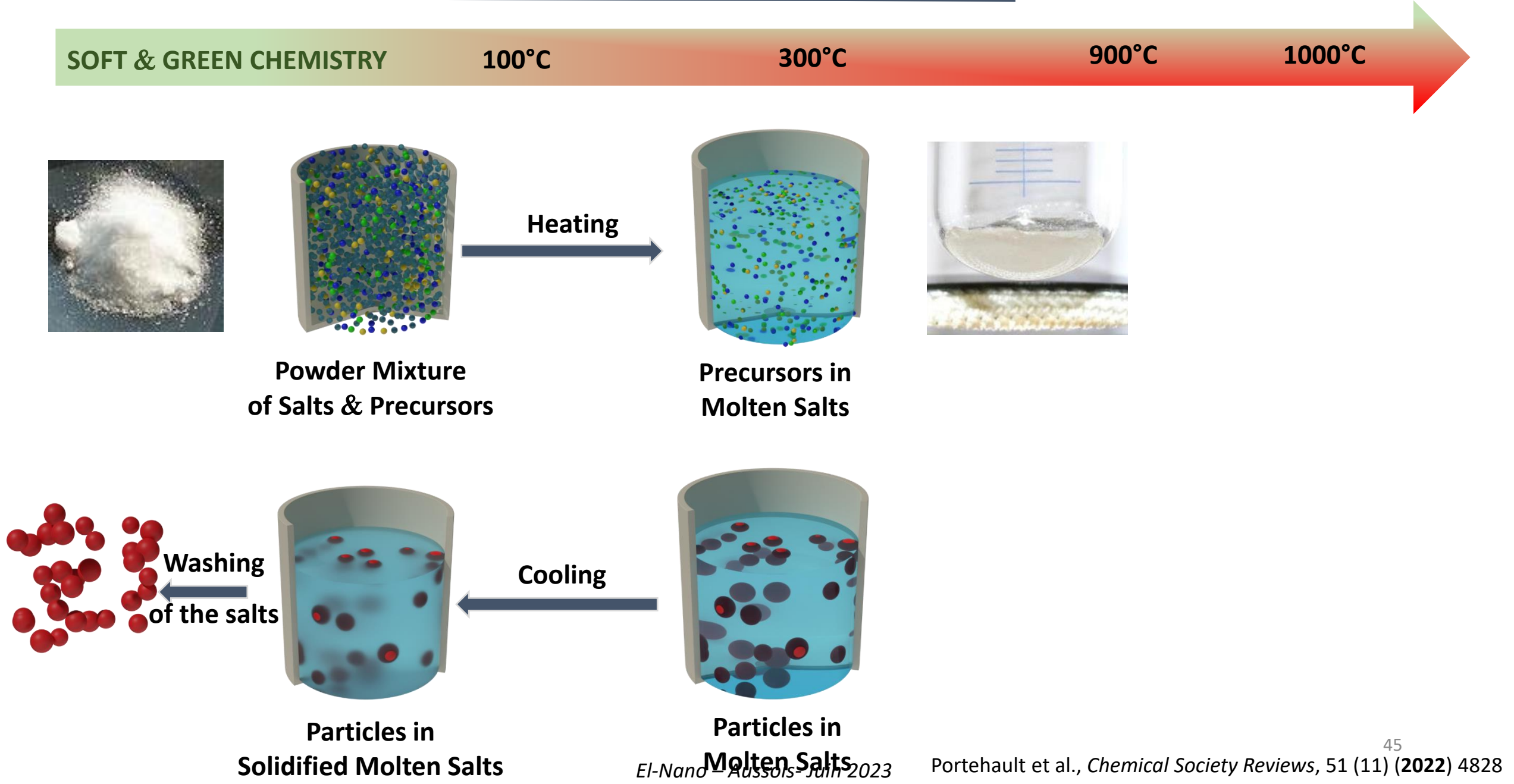


- ✓ Viscosity ~ water
- ✓ Stability ~ 900°C
- ✓ Negligible vapor pressure

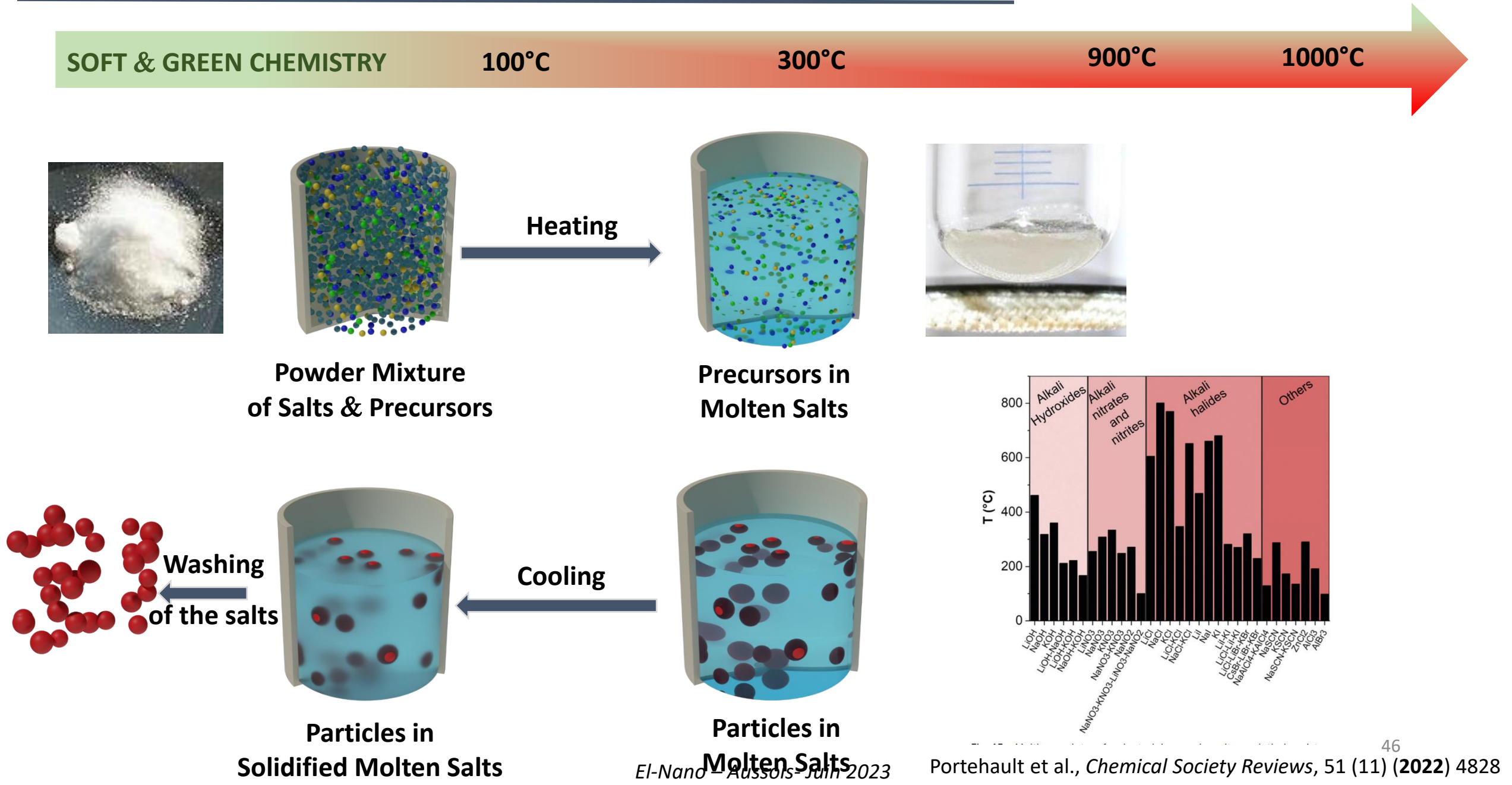


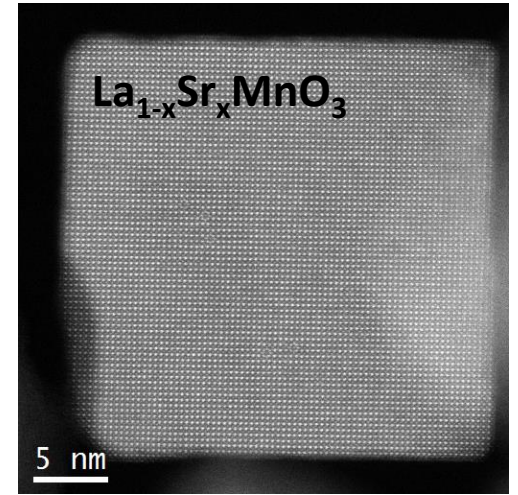
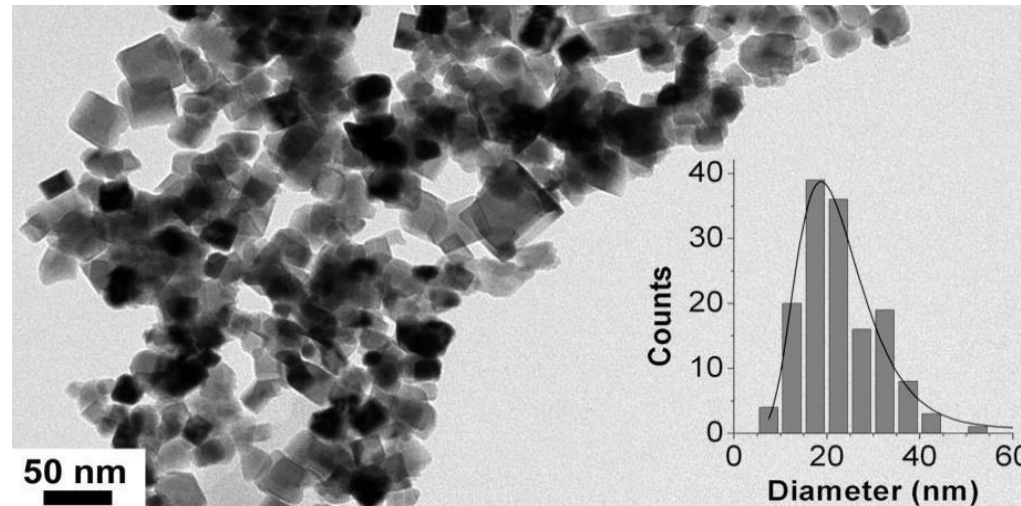
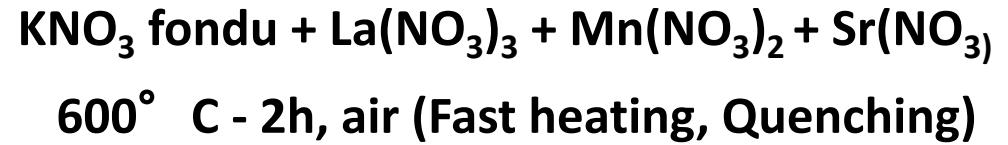
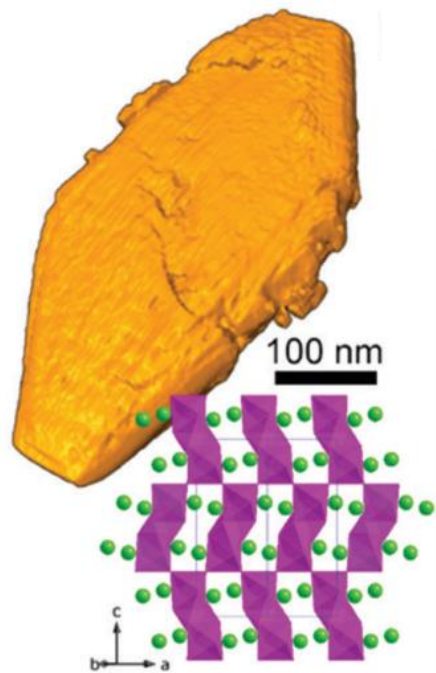
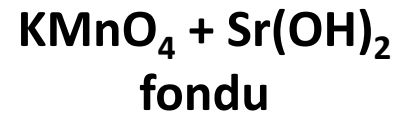


Chemistry of Nanomaterials : a fundamental bottleneck& one possible solution

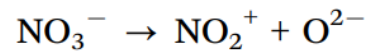


Chemistry of Nanomaterials : a fundamental bottleneck& one possible solution





H. Le Thi N'Goc, Adv. Mater., 29 (2017) 1604745

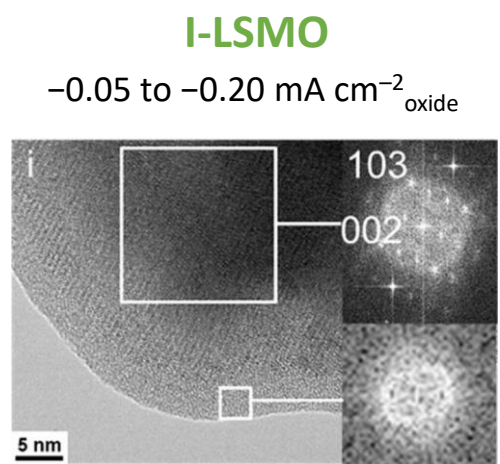
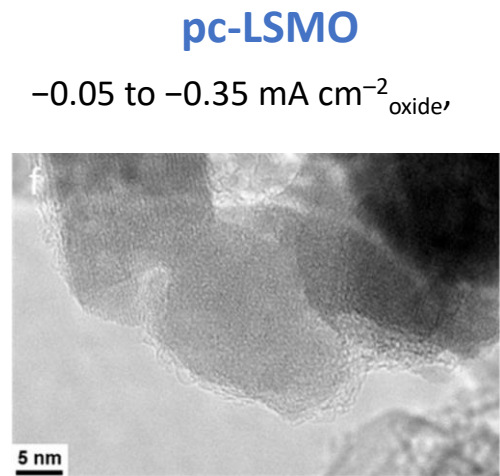
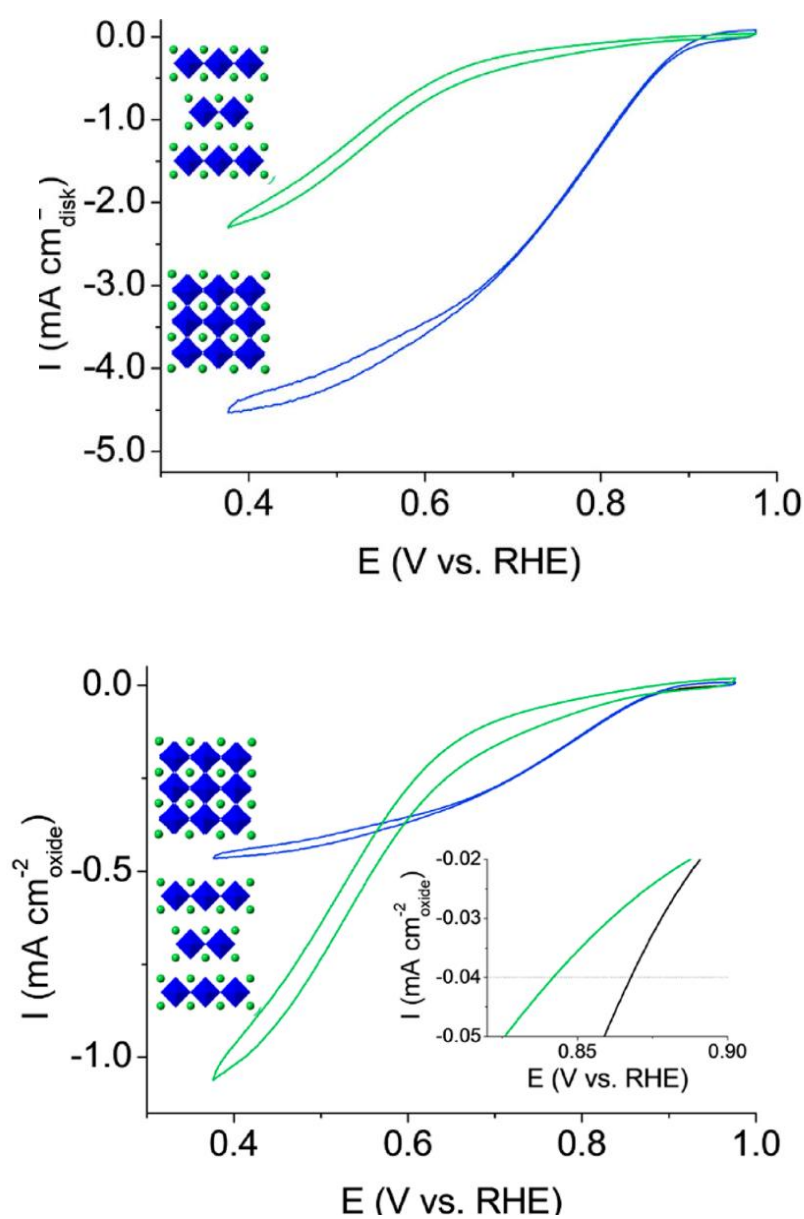
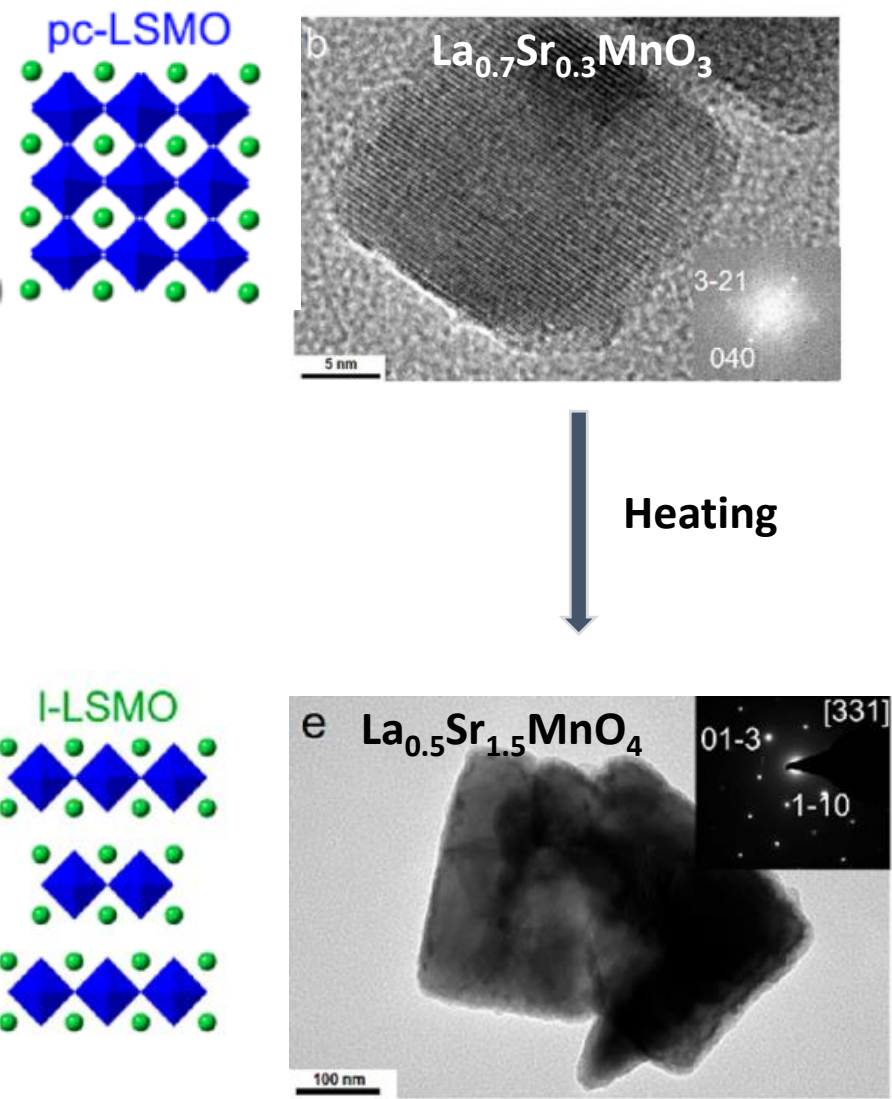


No organic ligands at the surface !

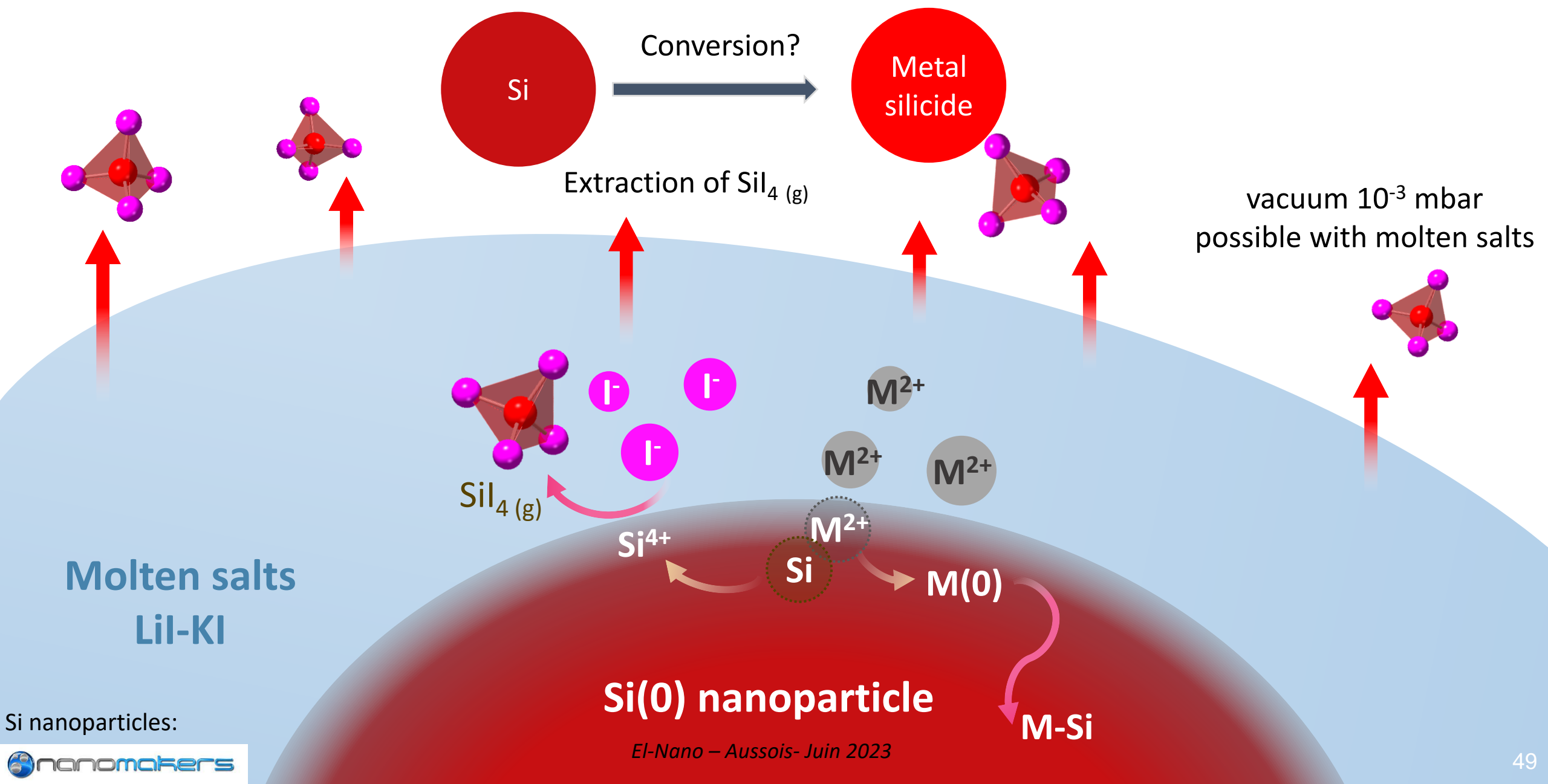
“ideal” composition and structure (XRD and TEM) : $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$

Easy substitution on A and B sites (Mn/Co)

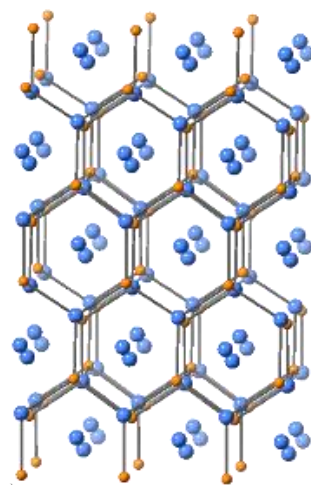
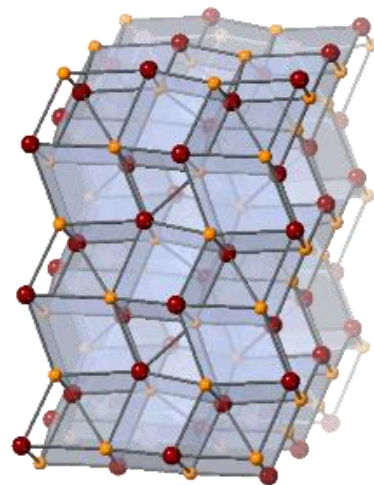
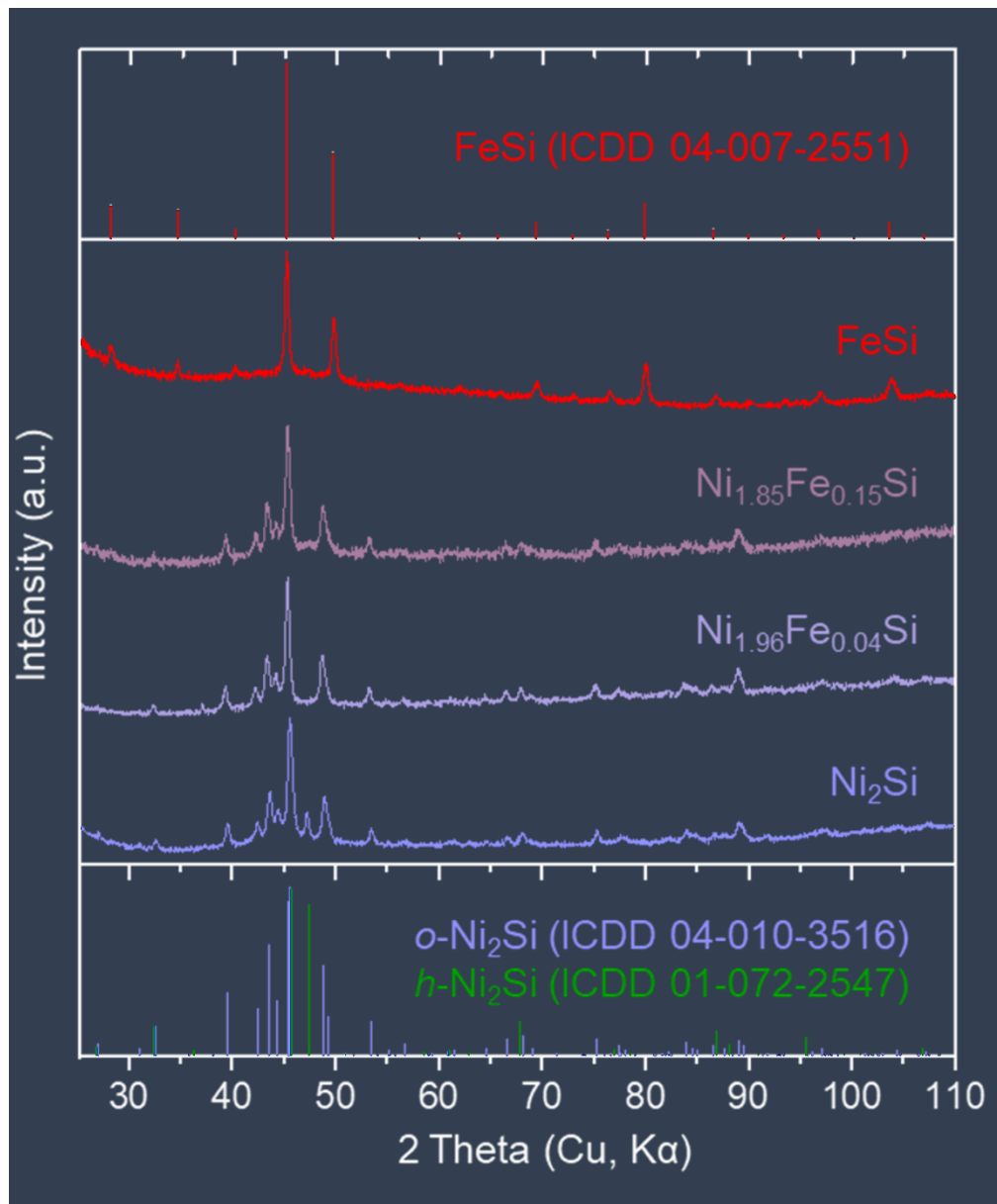
Nano-perovskite : Electrocatalysis (ORR)



Si Nano-particle as template : Multimetallic Silicide

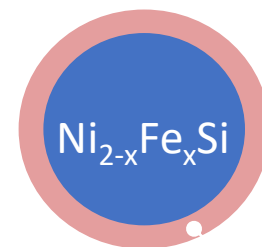


Multimetallic Silicide for Electrocatalysis (ORR)

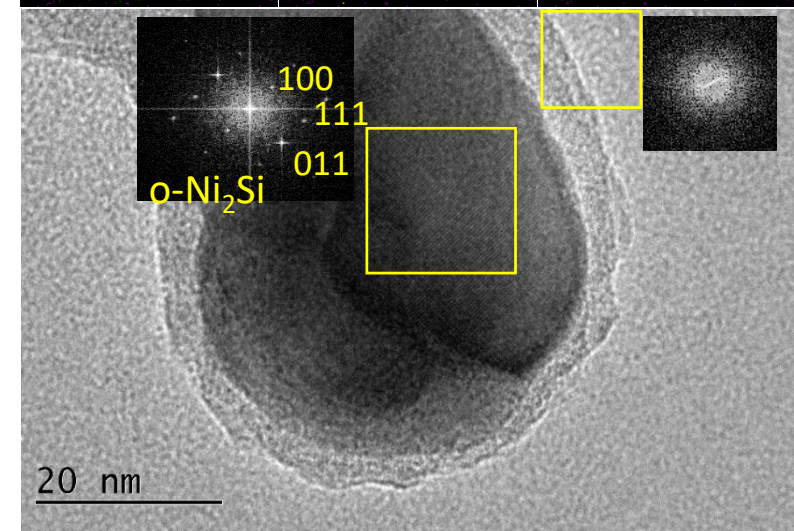
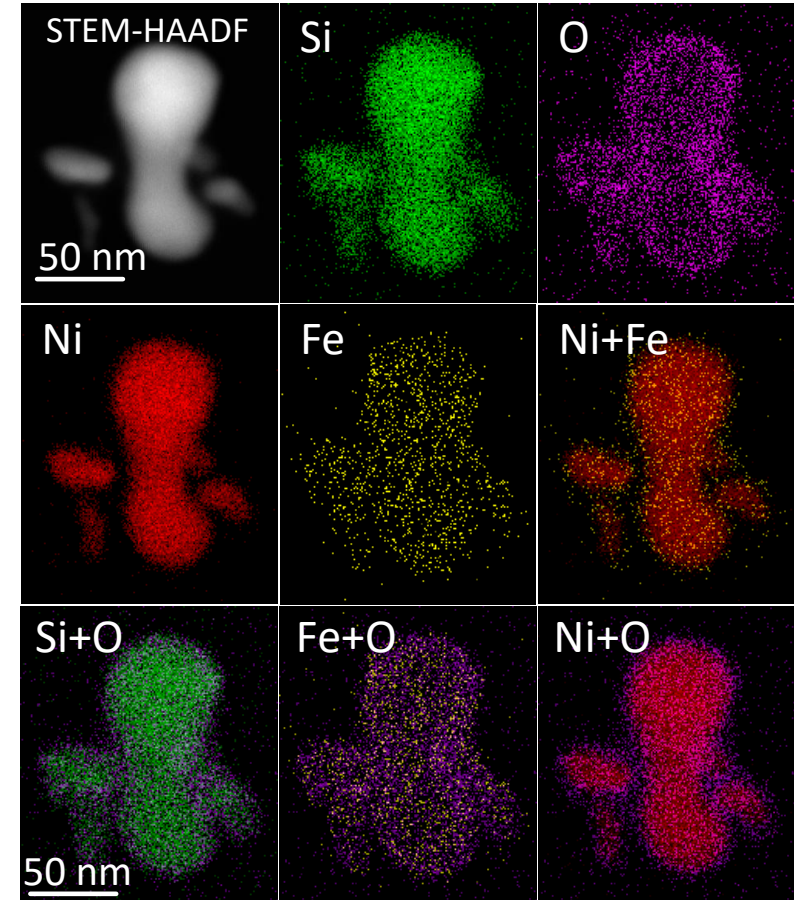


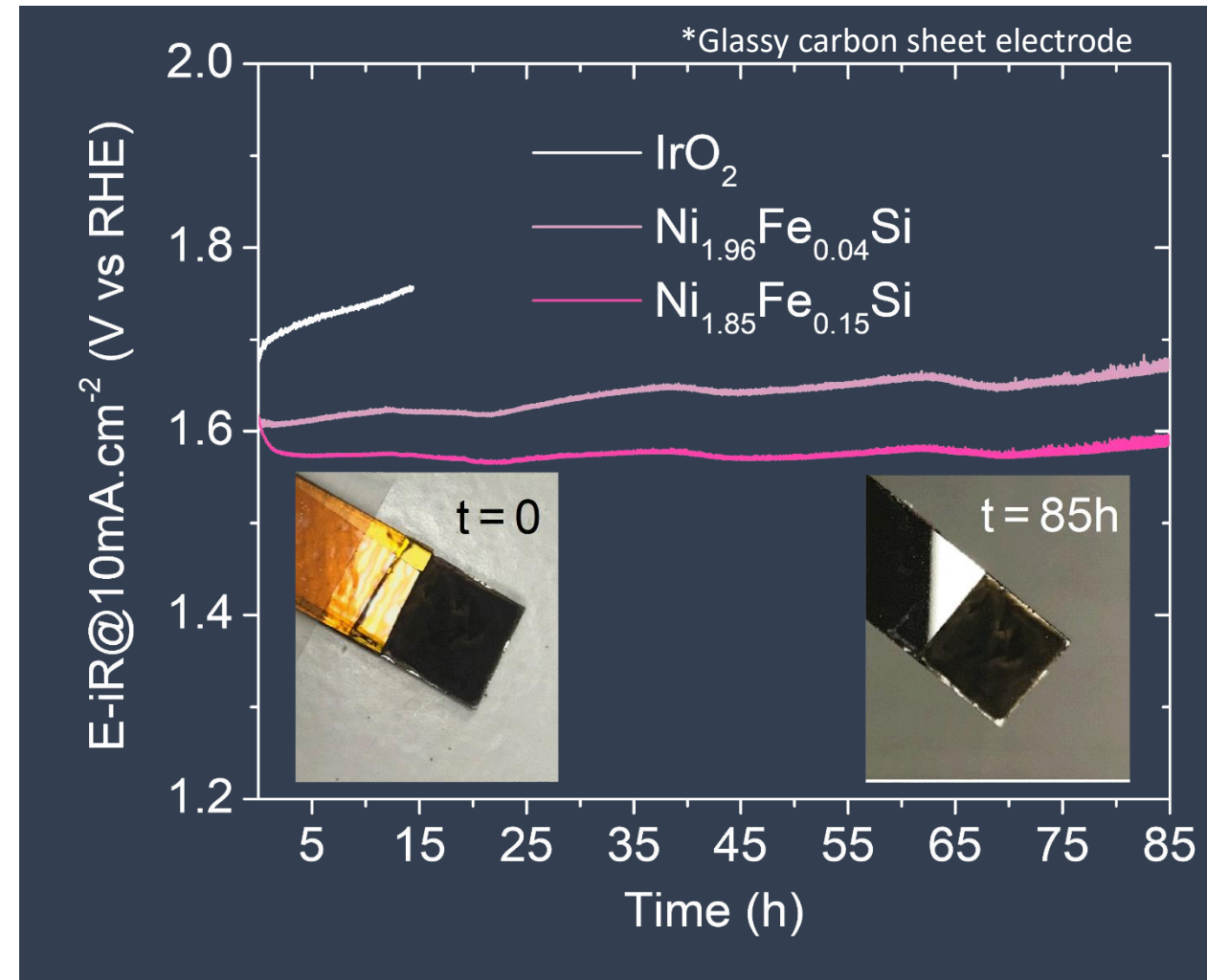
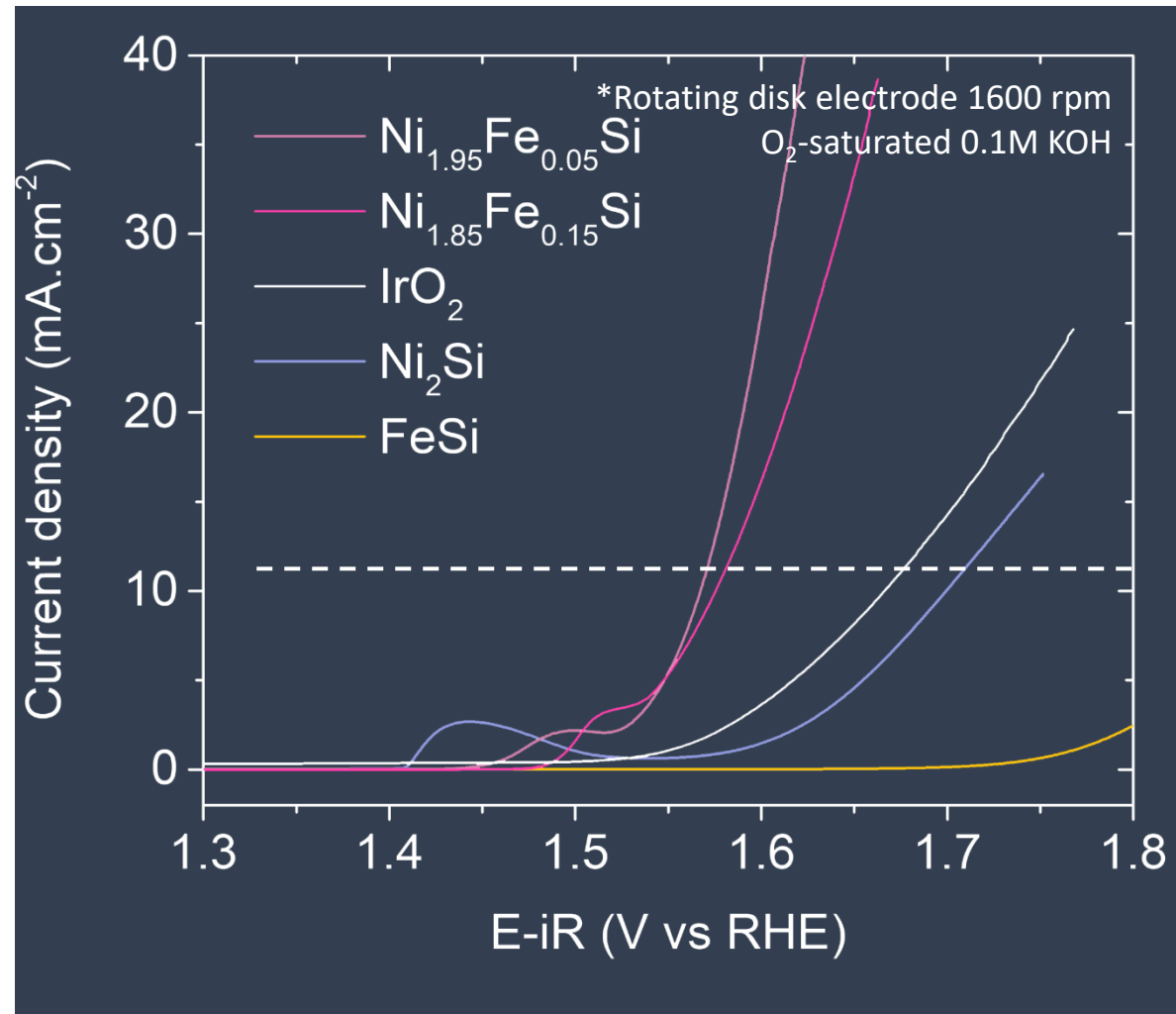
● Si ● Ni ● Fe

Fe-doped o-Ni₂Si



Oxidized
Ni, Fe and Si
(XPS)

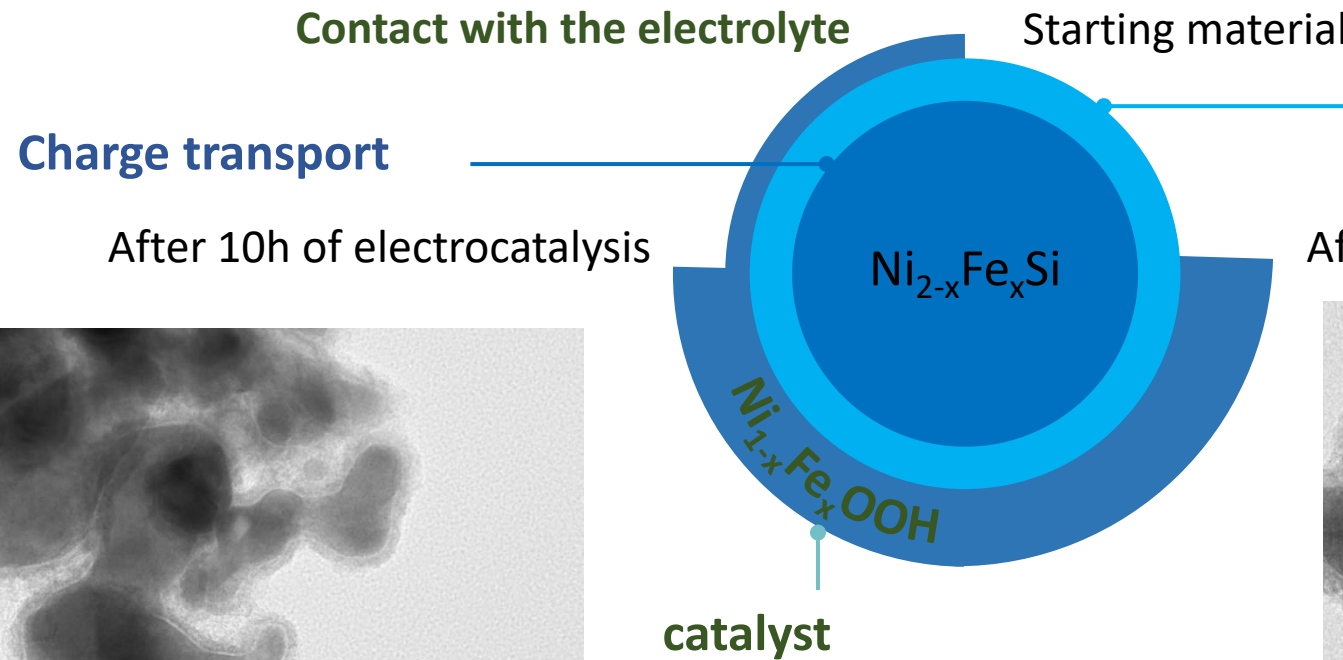




- ✓ NiFe silicides are highly active water oxidation electrocatalysts
- ✓ Activity stable for at least 85h

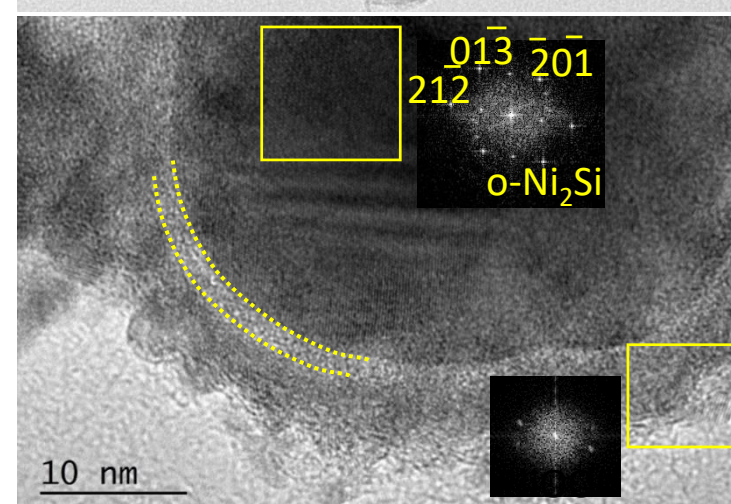
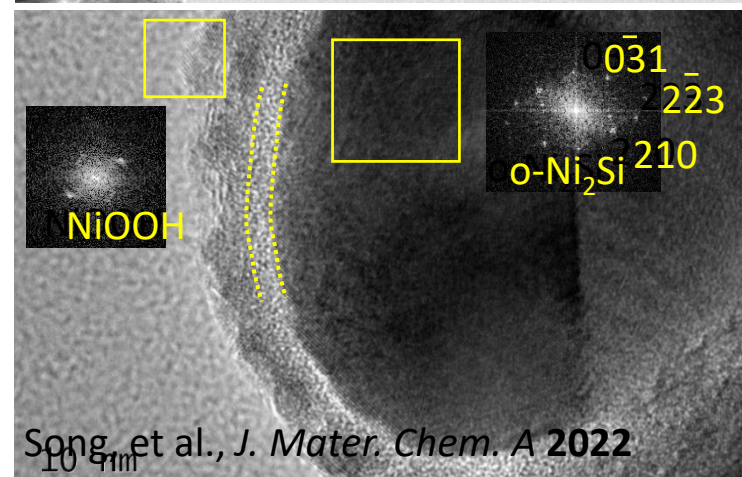
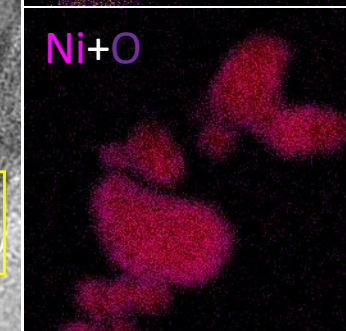
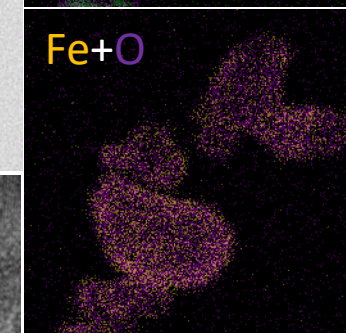
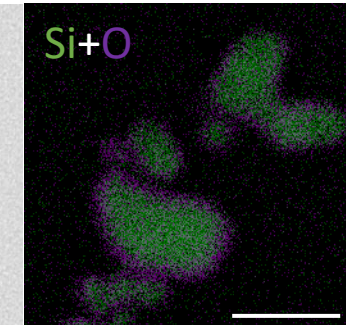
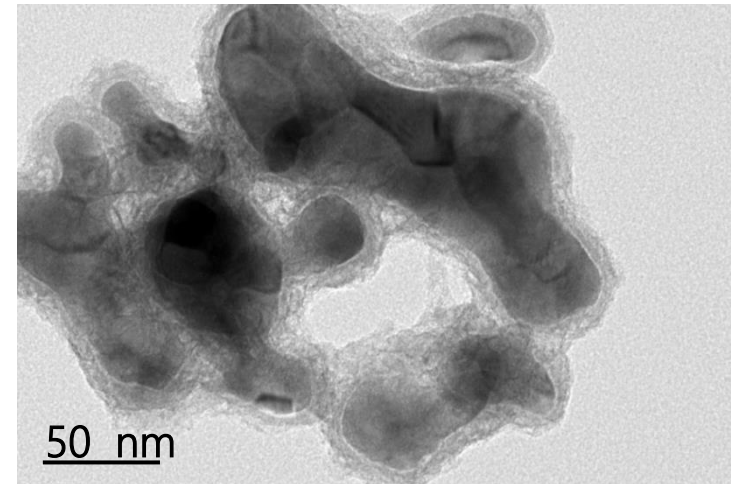
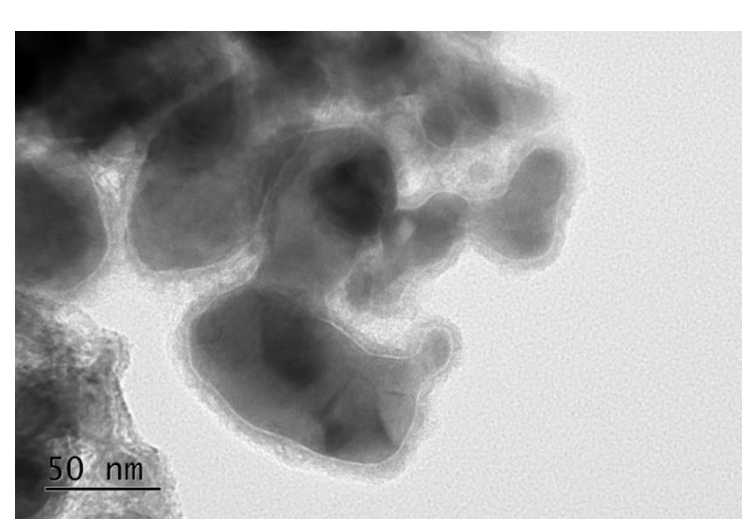
Multimetallic Silicide for Electrocatalysis (ORR)

- Metal & Si oxides (XPS)
- Passivates silicide core
- Enables charge transport

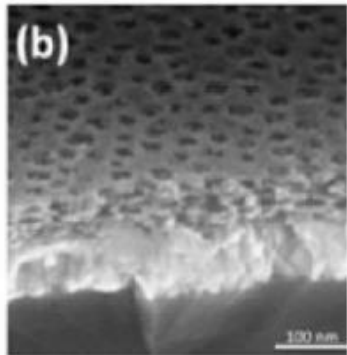


After 10h of electrocatalysis

After 85h of electrocatalysis

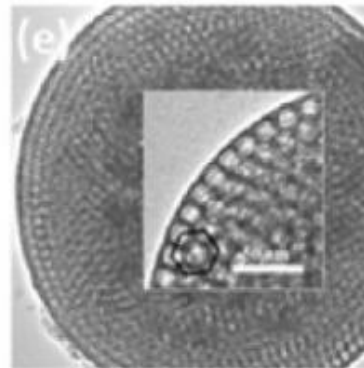
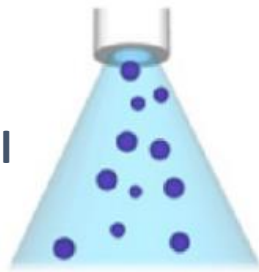


Dip-coating

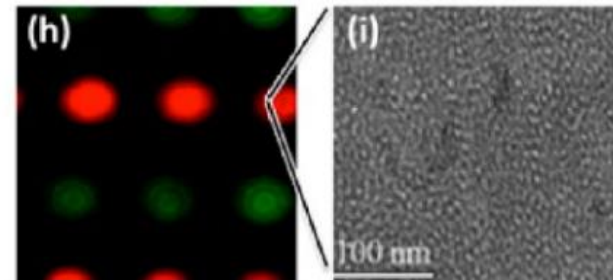
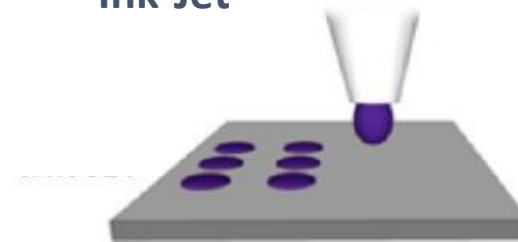


Molecular Sol-Gel

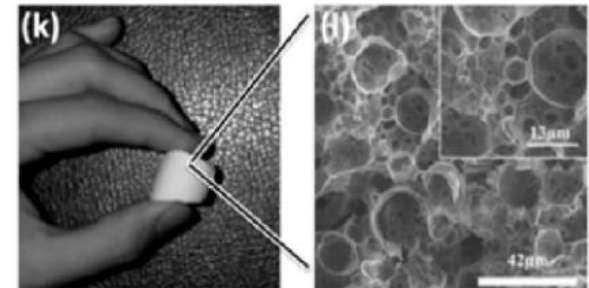
Aerosol



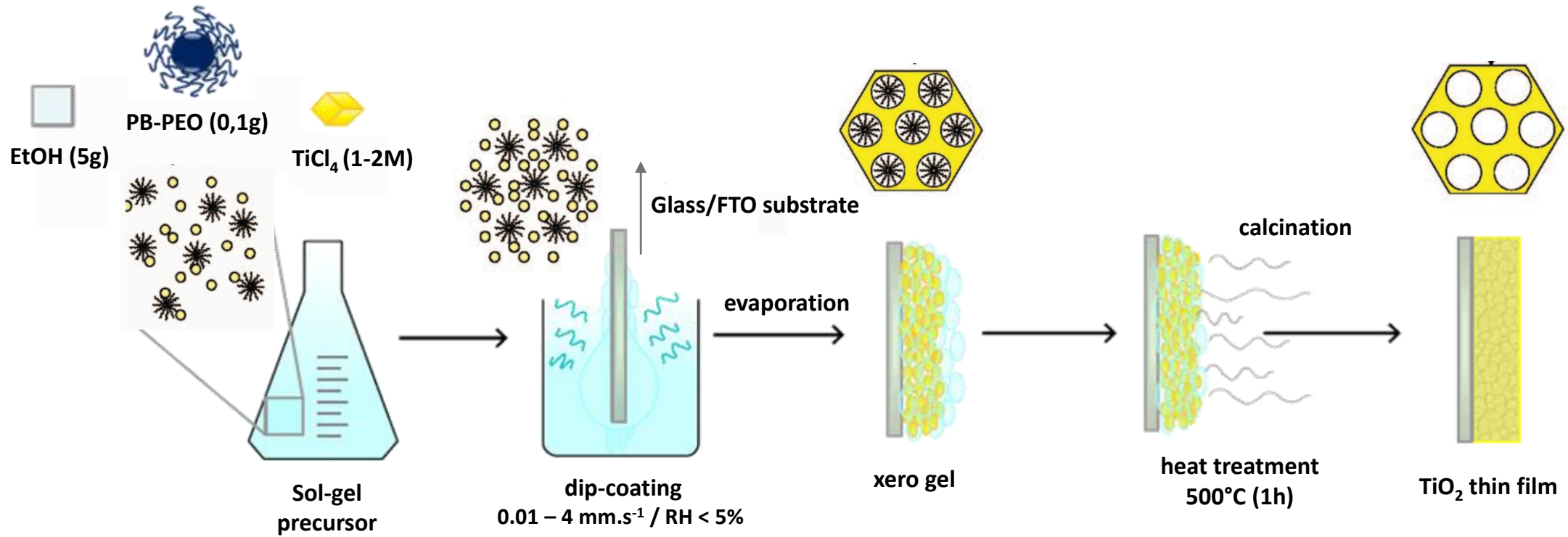
Ink-Jet



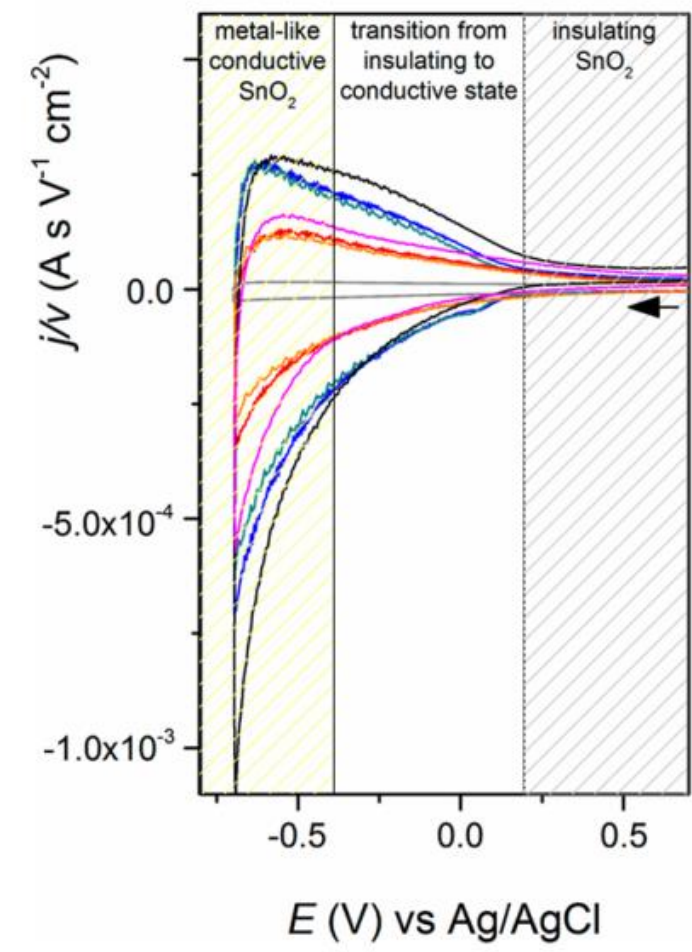
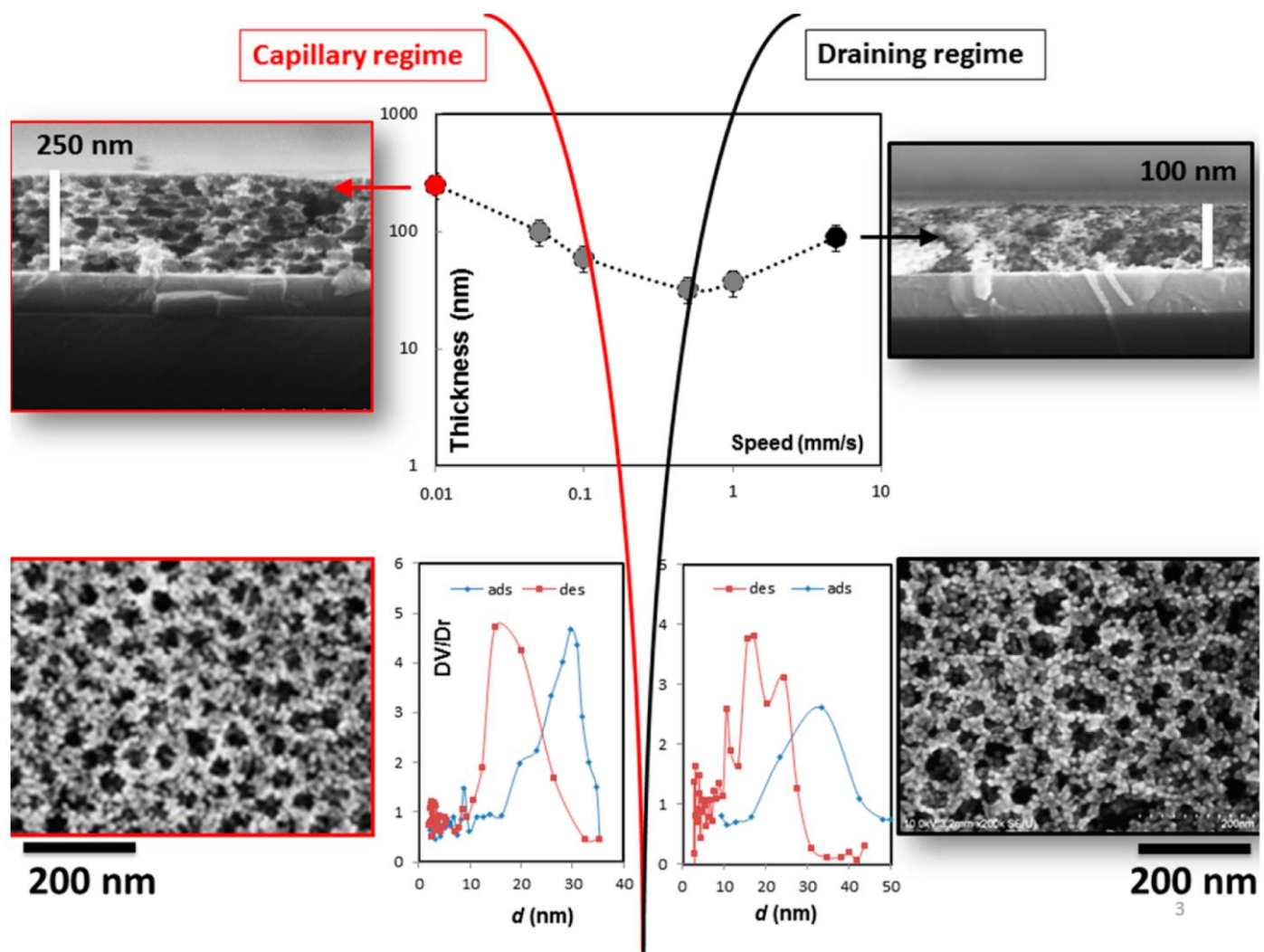
Foaming Process



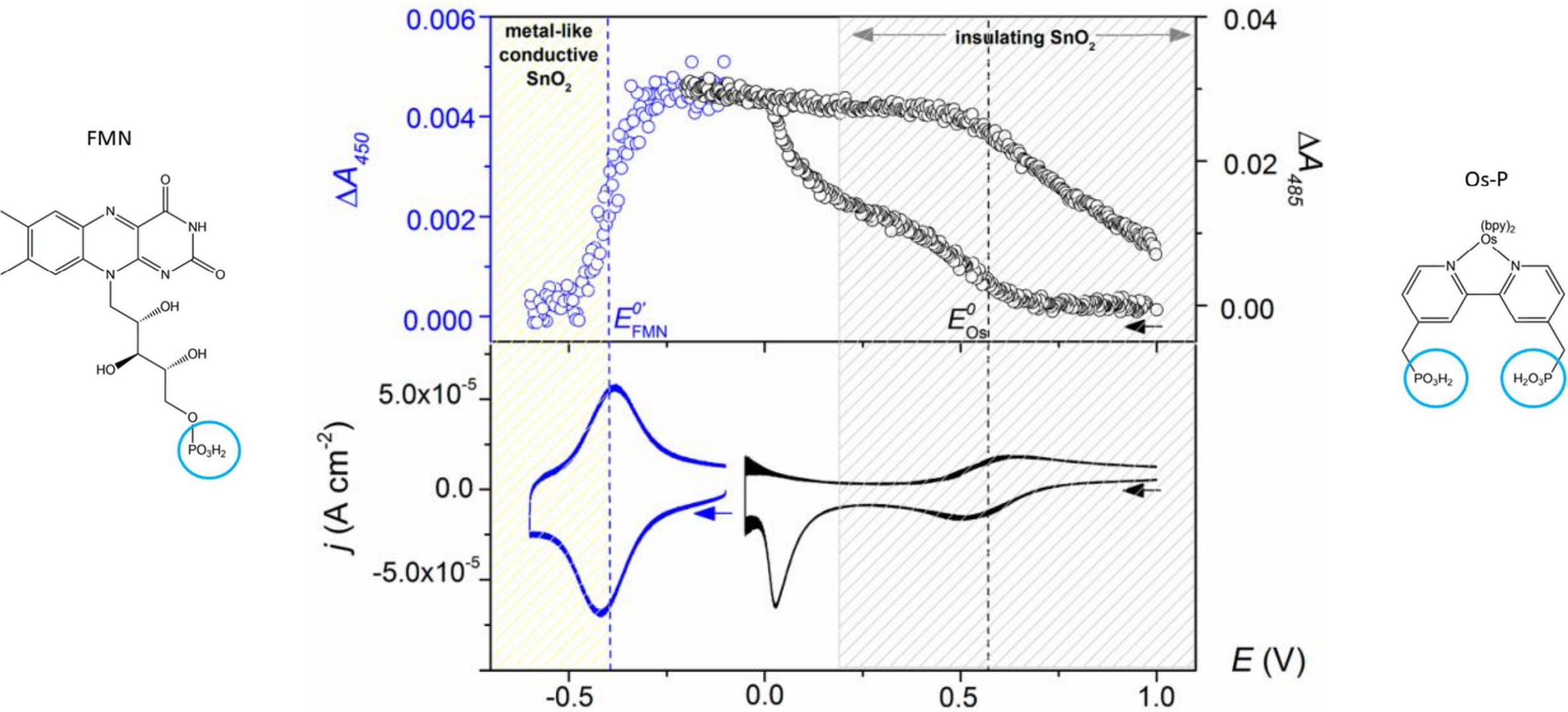
Porous and Hierarchically Structure : Combining Synthesis and Processing



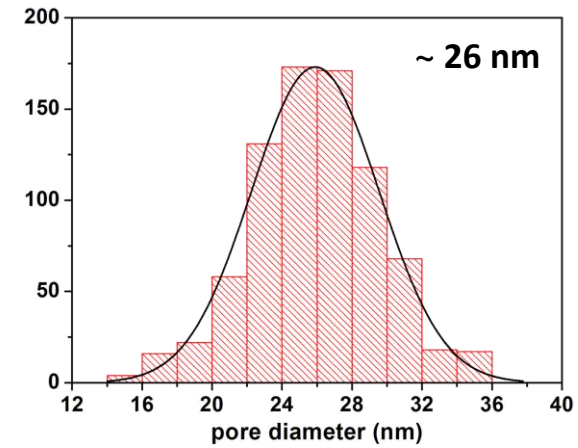
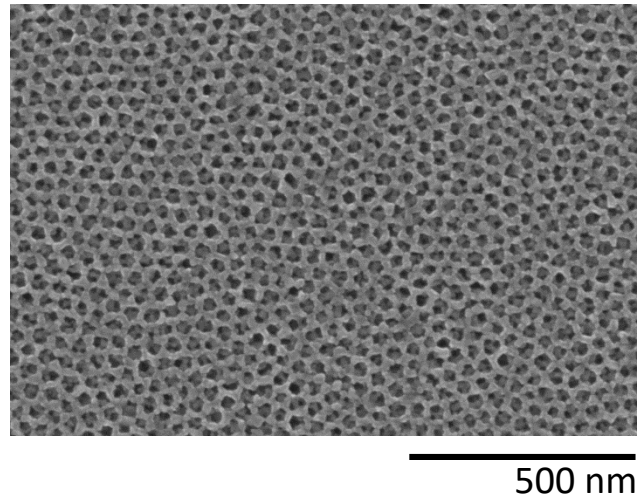
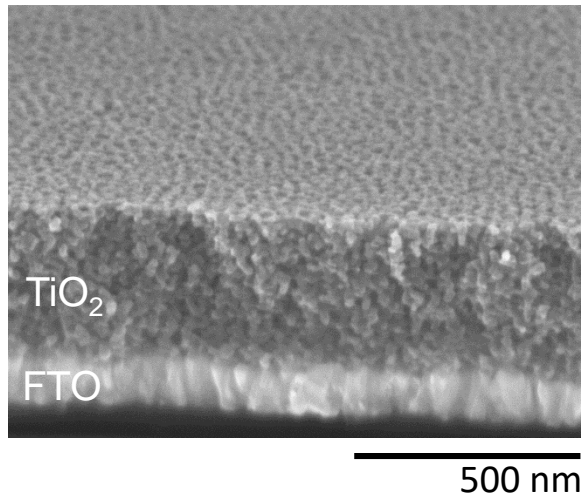
Controlling the Thickness by playing with the Withdrawn Speed : Case of SnO₂



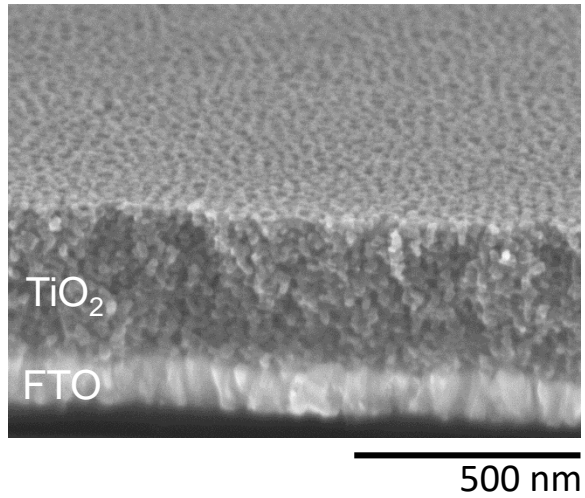
Use the Important Solid/Electrolyte Interface to Adsorb Molecules



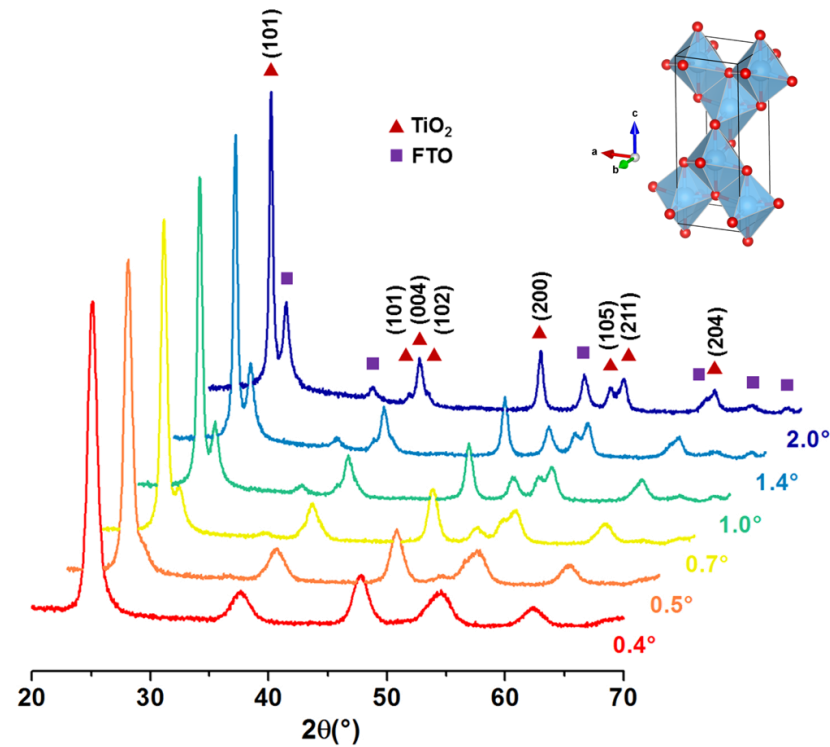
Typical electrode architecture



Typical electrode architecture

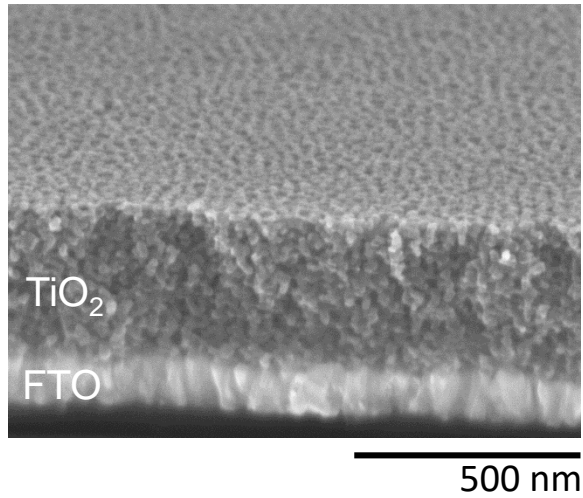


Glancing-angle XRD

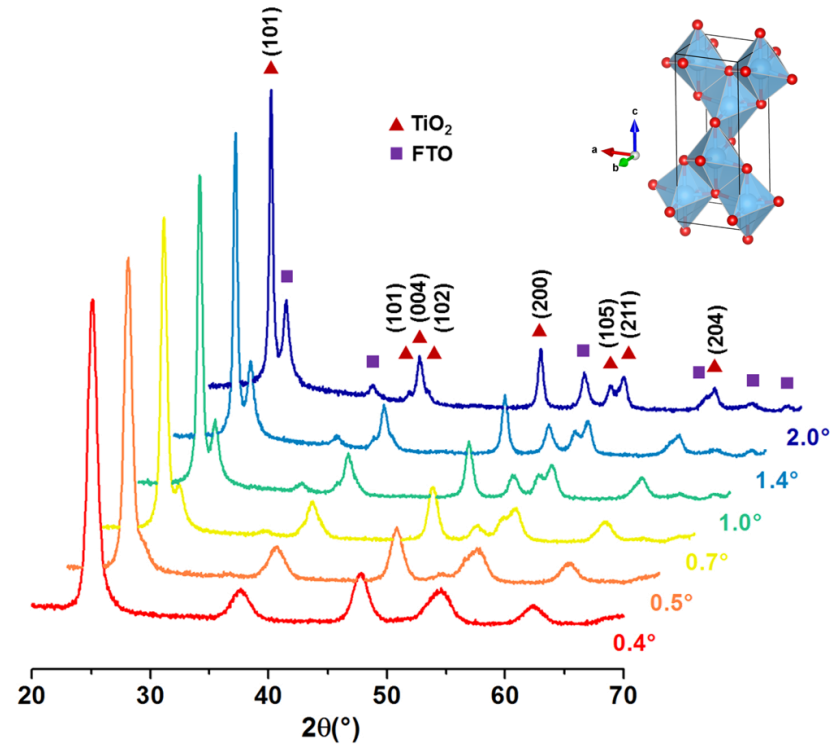


TiO_2 anatase
Homogeneous crystallite size ~ 10 nm

Typical electrode architecture

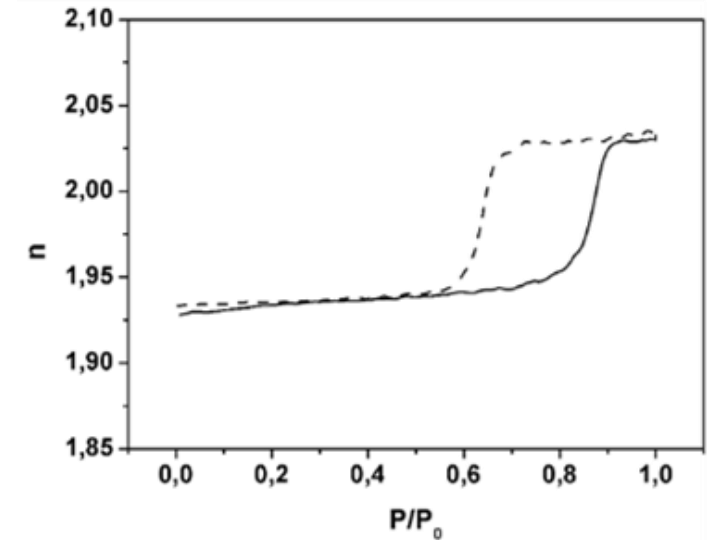


Glancing-angle XRD



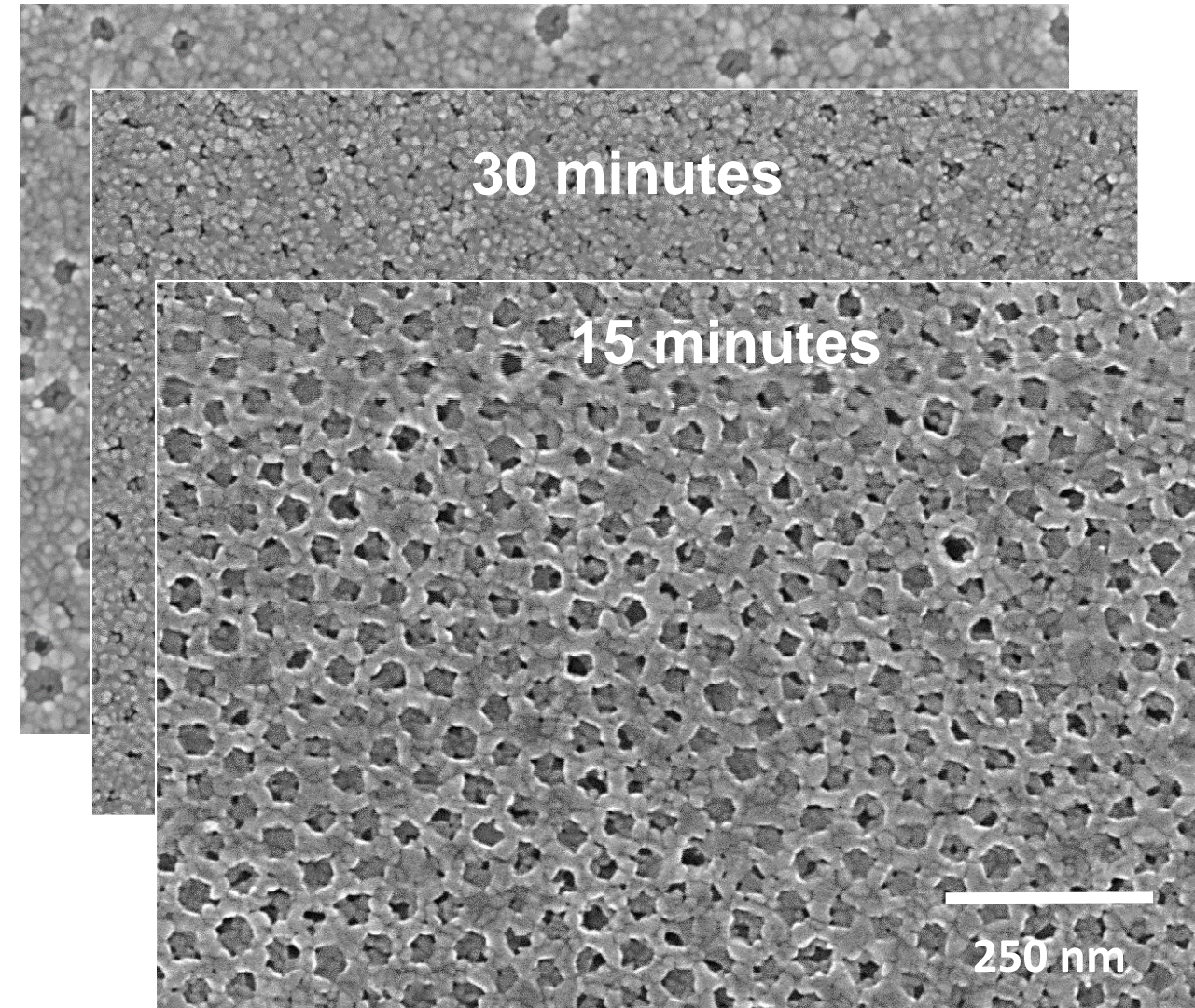
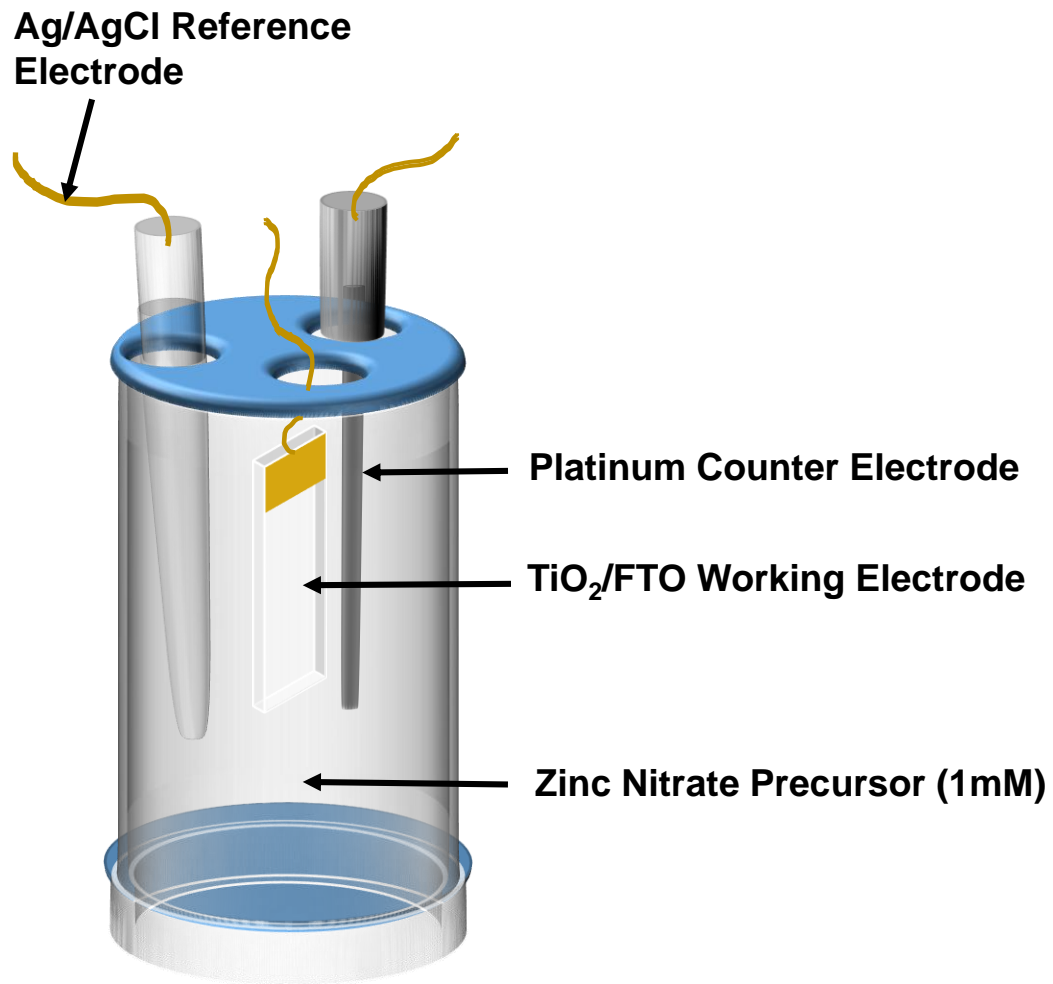
TiO_2 anatase
Homogeneous crystallite size ~ 10 nm

Environmental Ellipsometric Porosimetry

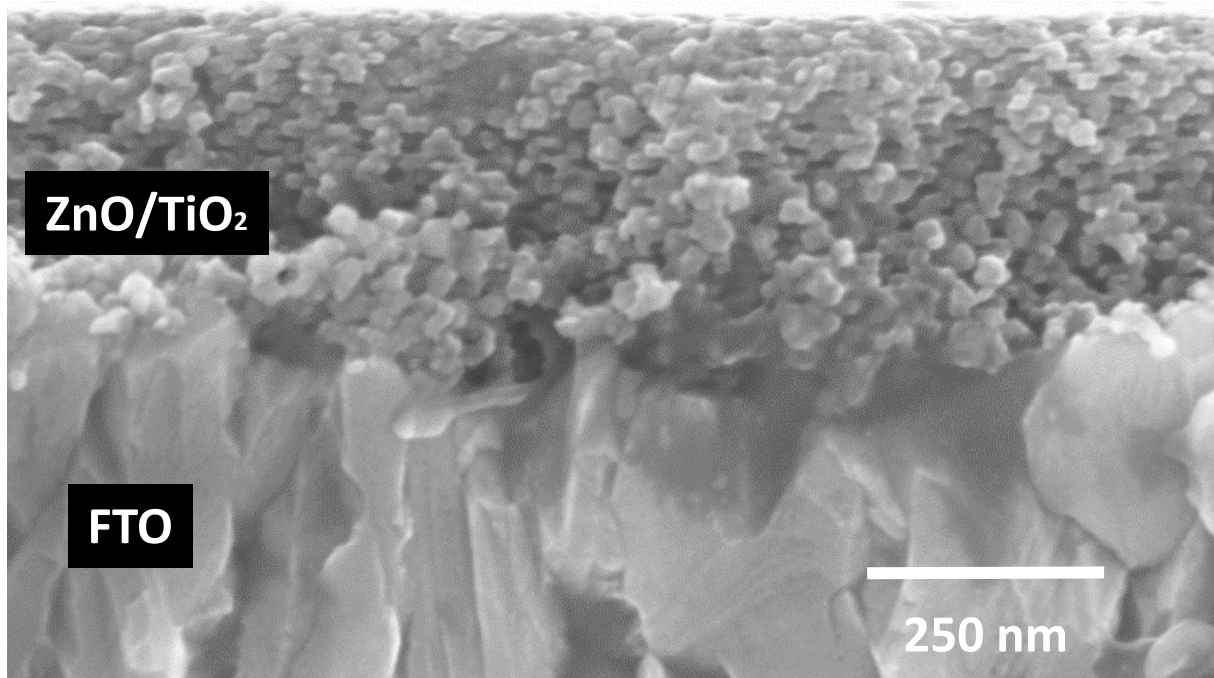


Average porosity $\sim 20\%$
Pore diameter ~ 26 nm

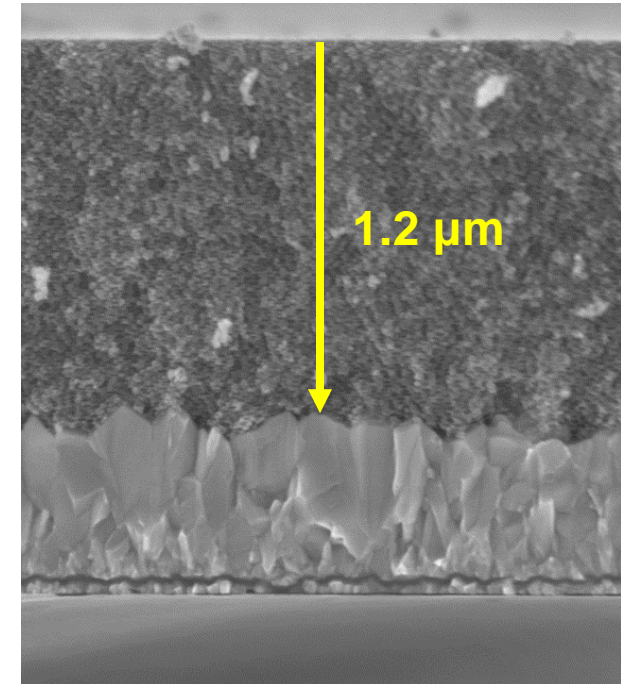
Porous and Hierarchically Structure to fabricate Heterostructure



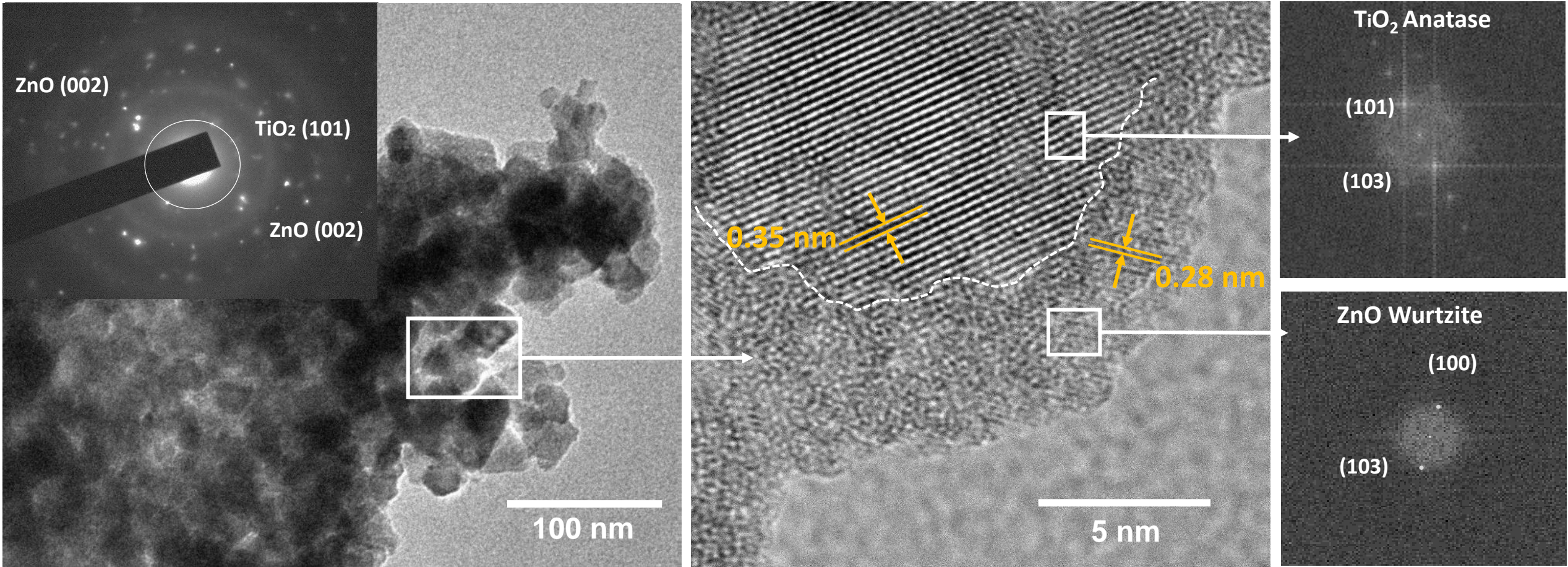
ZnO/TiO₂/FTO 15 Minutes Deposition



8 Layers



EDS measurements:
Ti : Zn = 1:0.02
atomic (%)



TEM/Electronic Diffraction

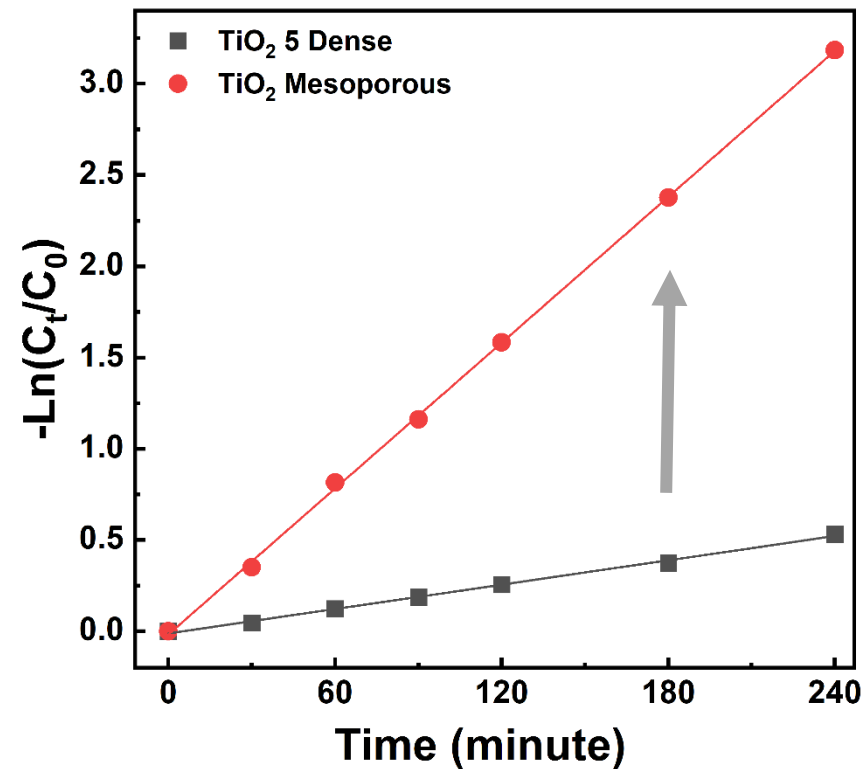
HRTEM

FFT

Photodegradation of Methylene Blue

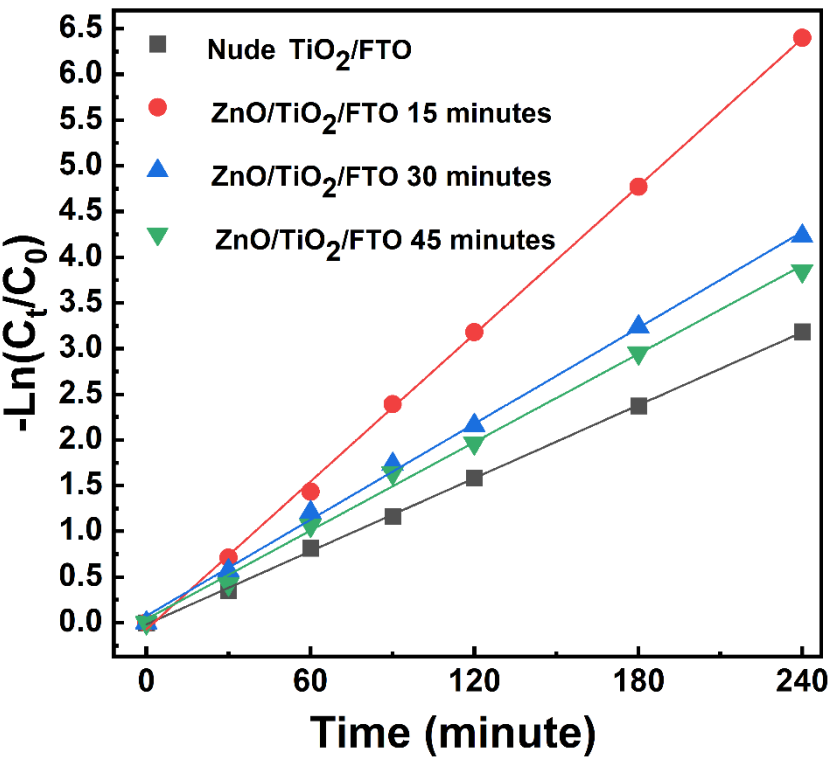
Irradiation Source: **UVA ($\lambda = 365\text{nm}$)**

Effect of Structuration

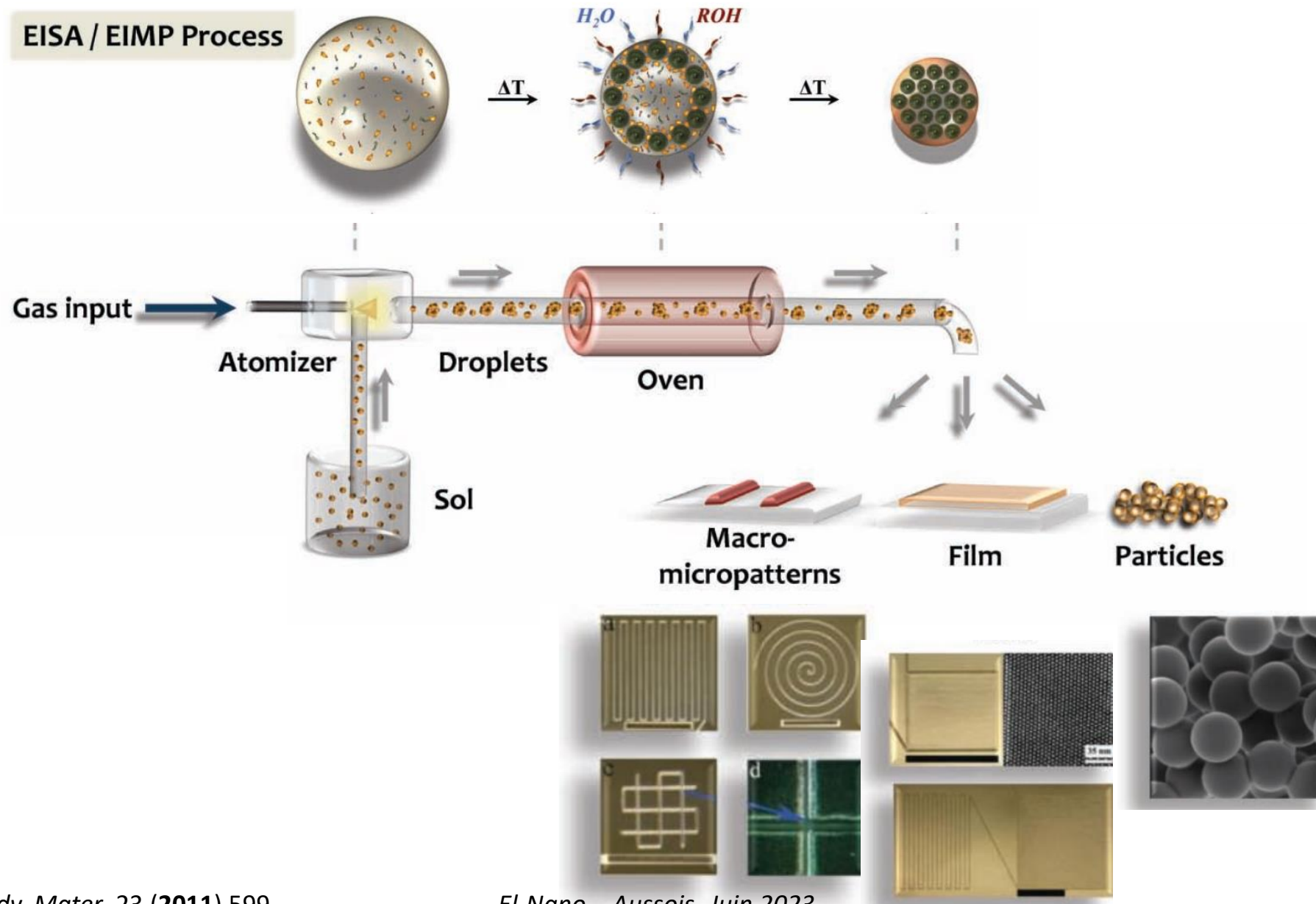


Pseudo-first-order kinetic model

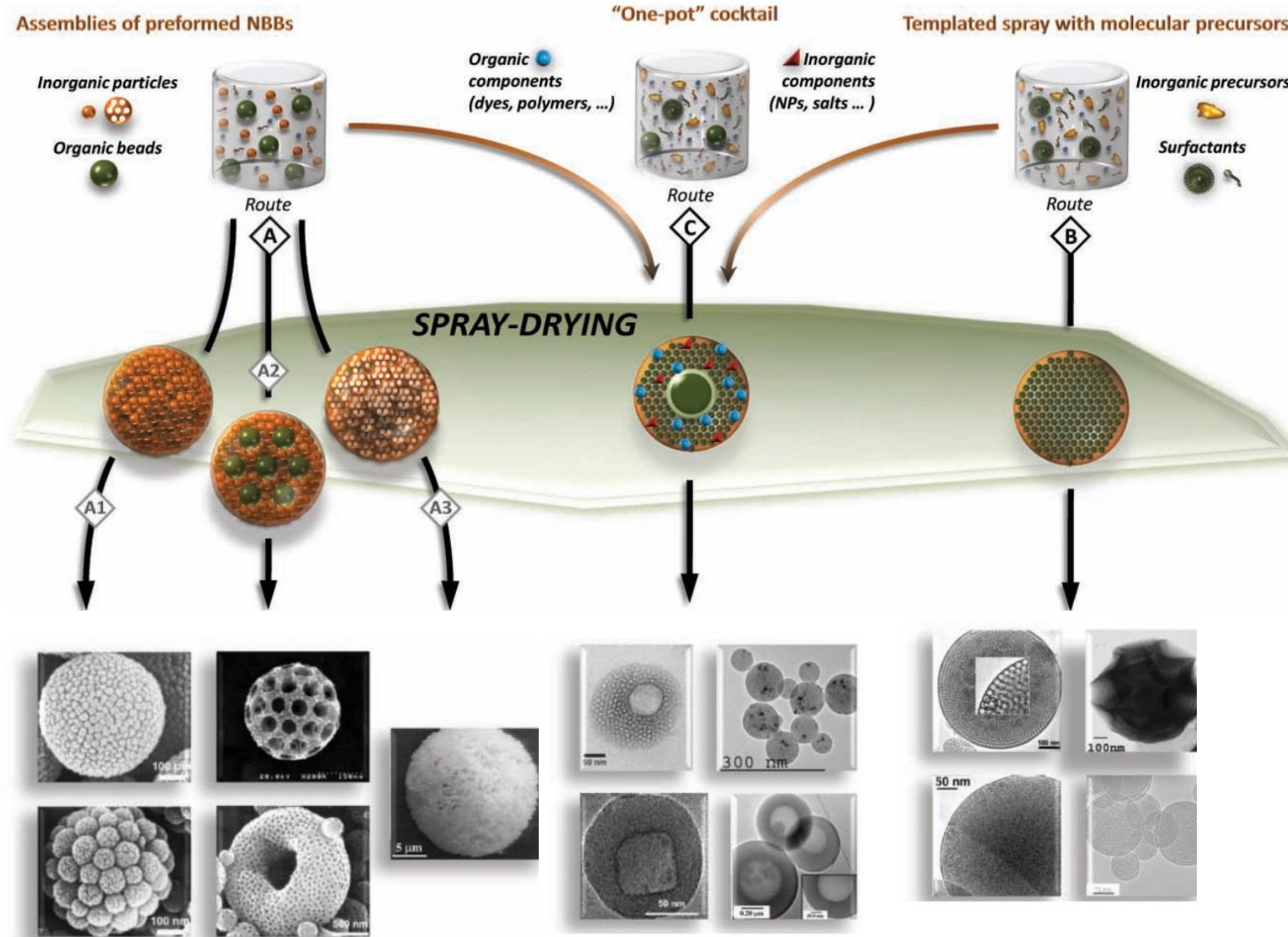
Effect of electrodeposition time



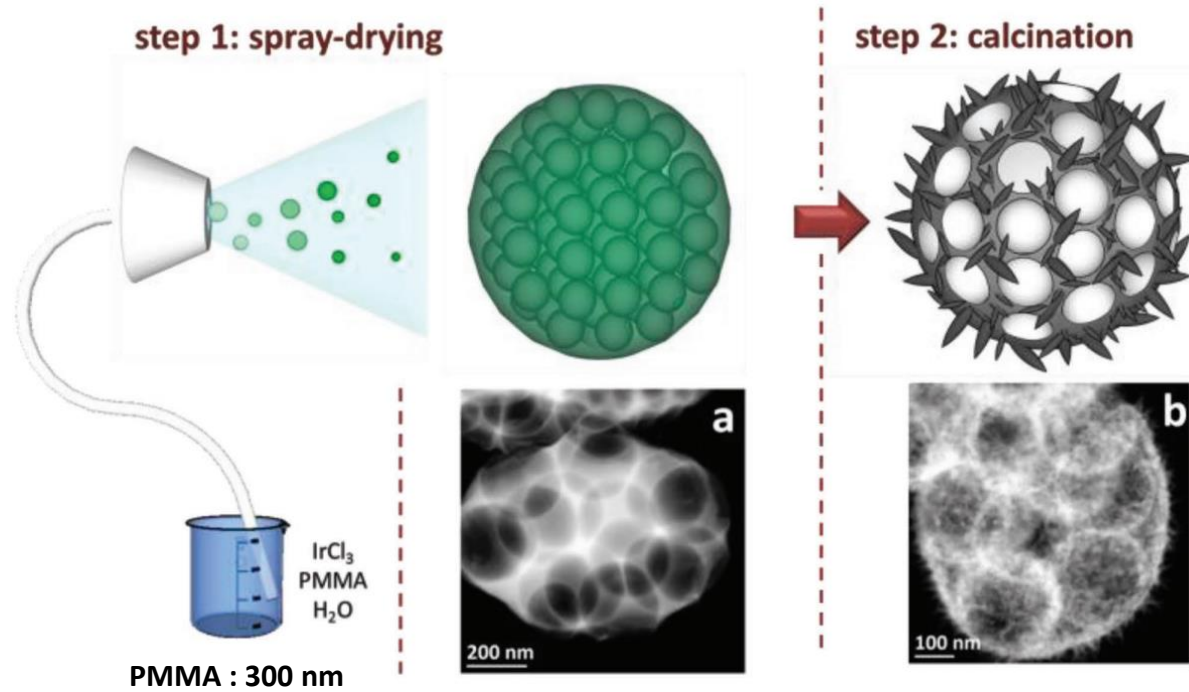
Sol-gel Chemistry coupled with Aerosol Approaches to Fabricate Macro- micropatterns, Film and Particles



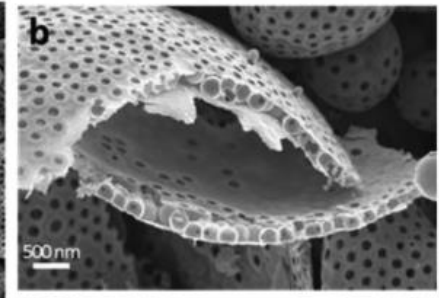
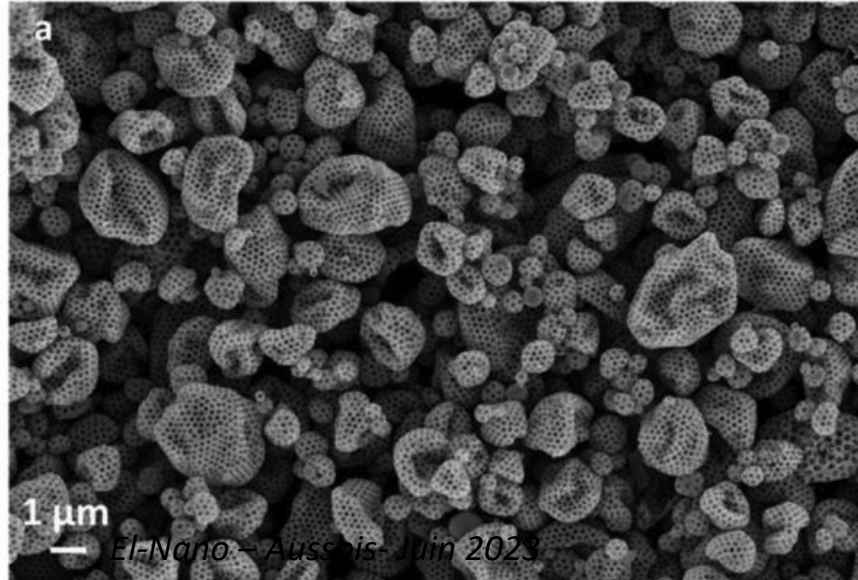
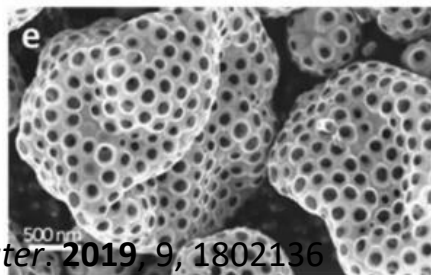
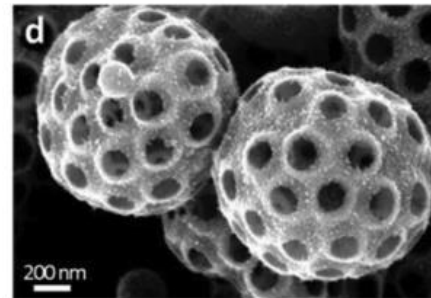
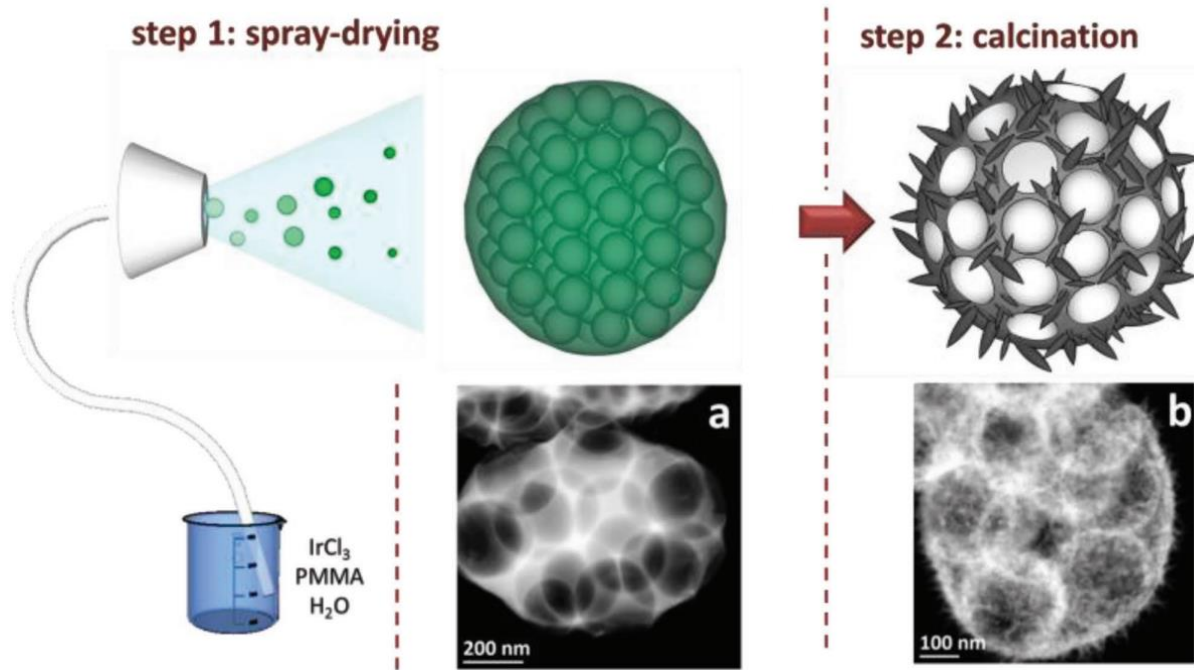
Strategies to Synthesize Porous Particles



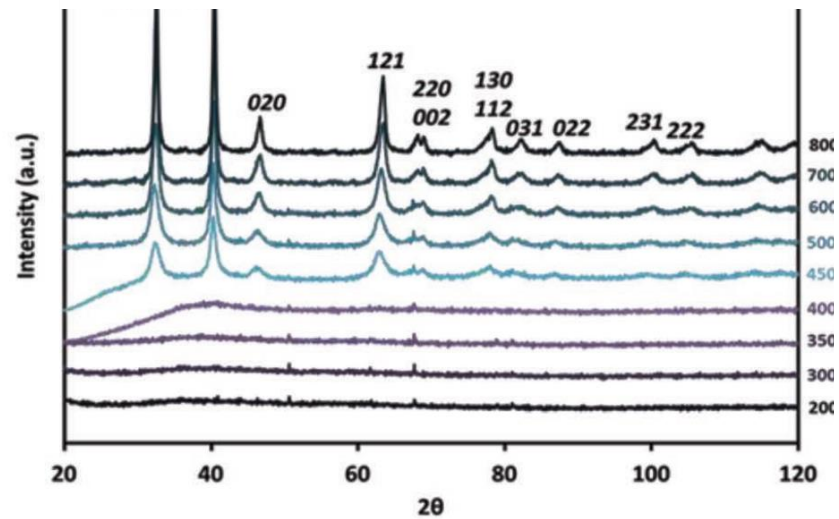
Design of Macroporous Sphere of Electrocatalyst : IrO₂-based electrocatalyst



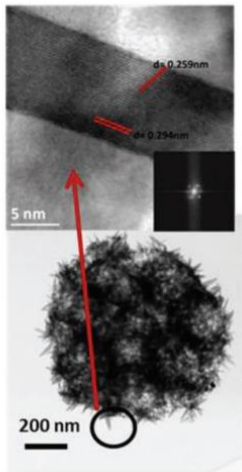
Design of Macroporous Sphere of Electrocatalyst : IrO₂-based electrocatalyst



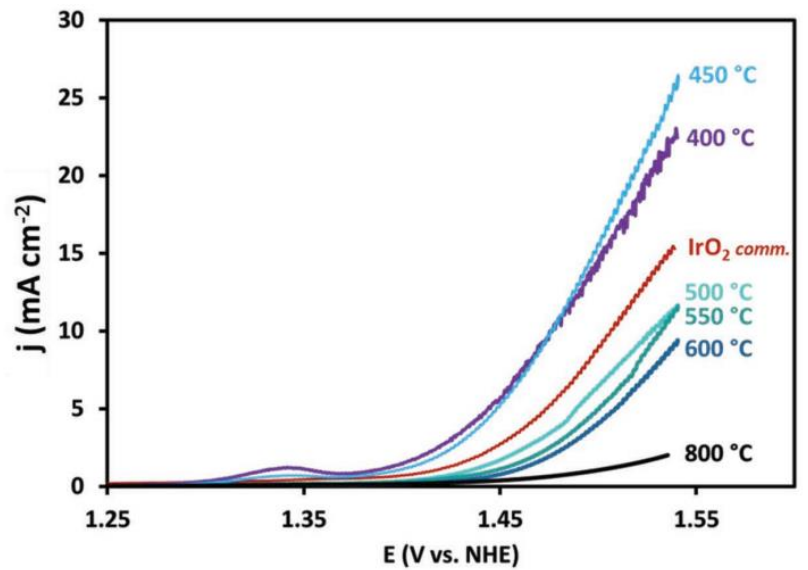
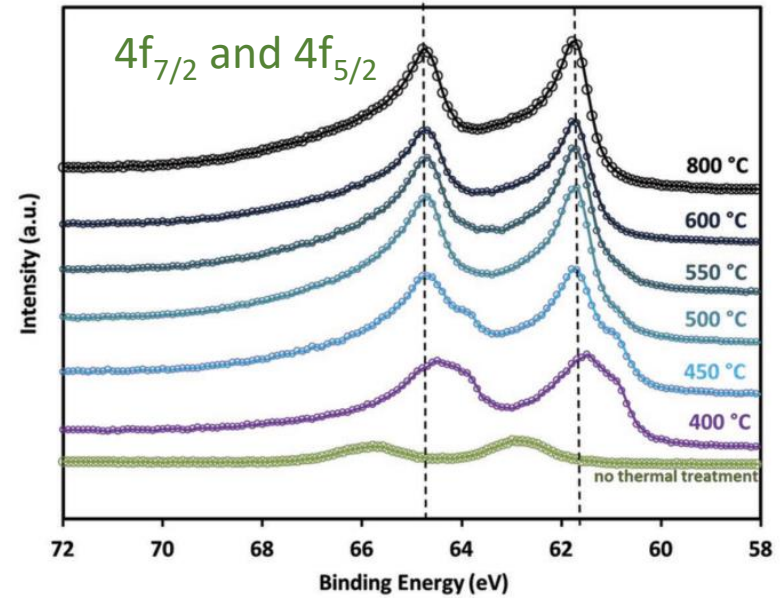
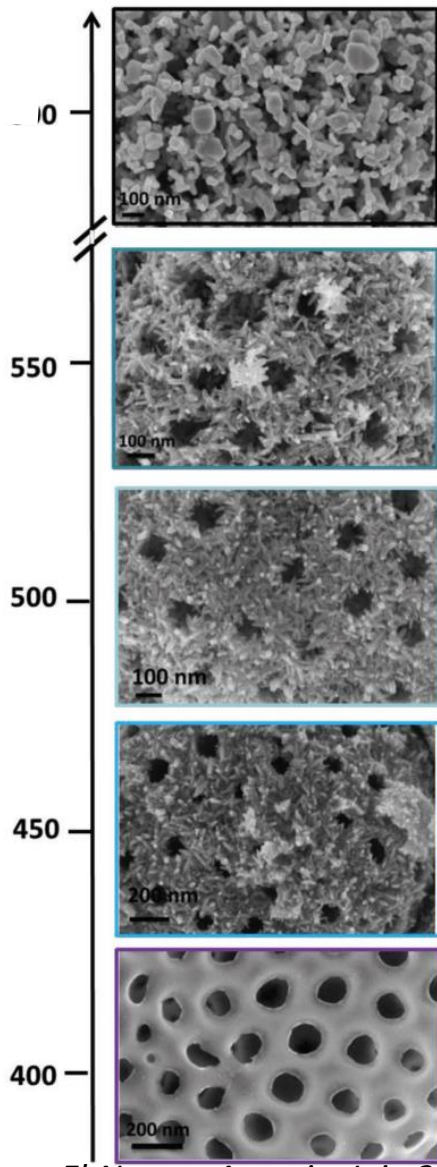
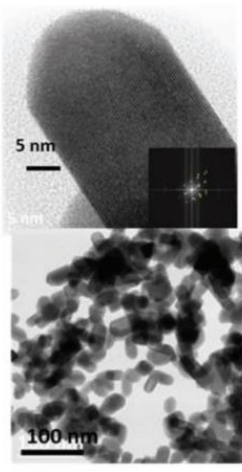
Design of Macroporous Sphere of Electrocatalyst : IrO₂–based electrocatalyst



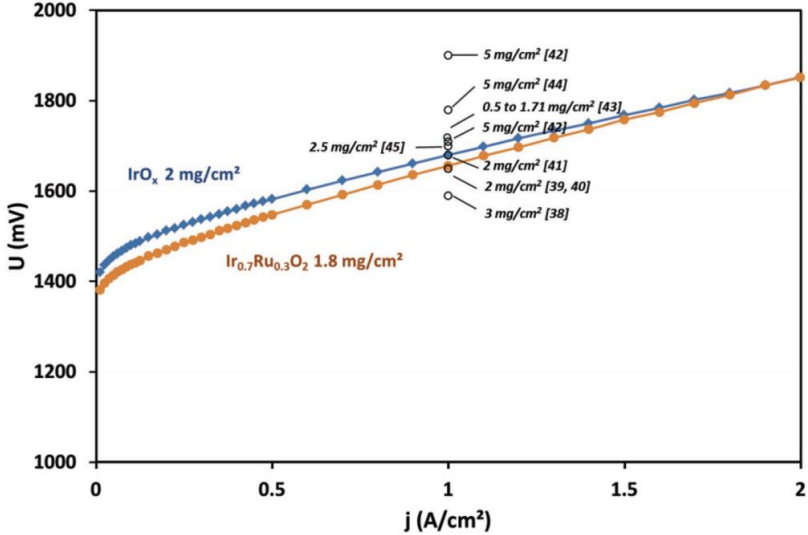
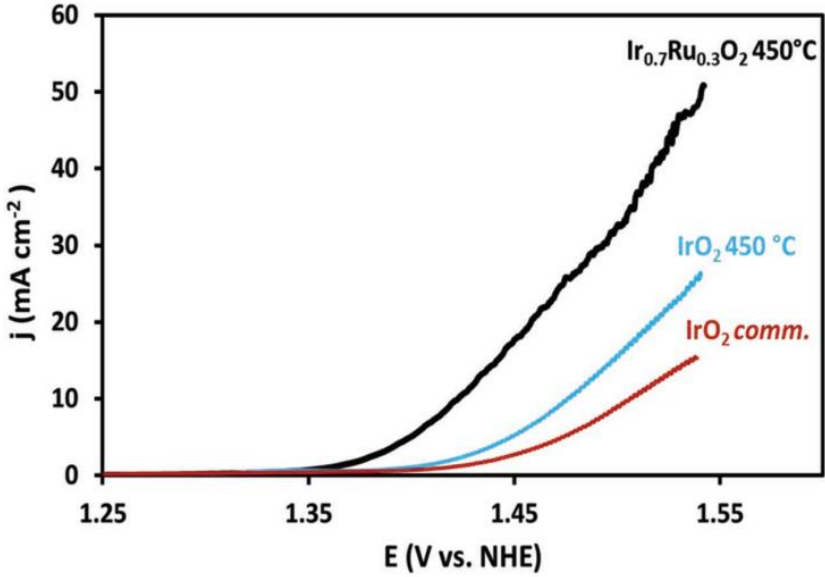
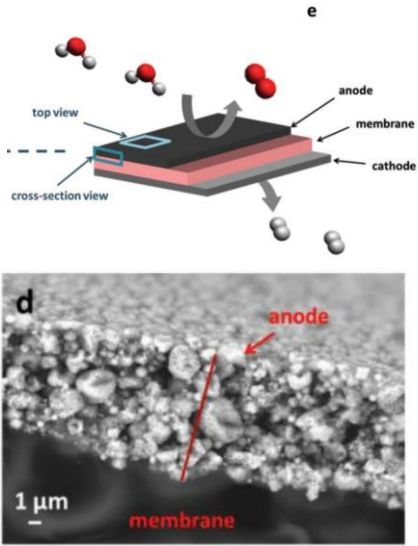
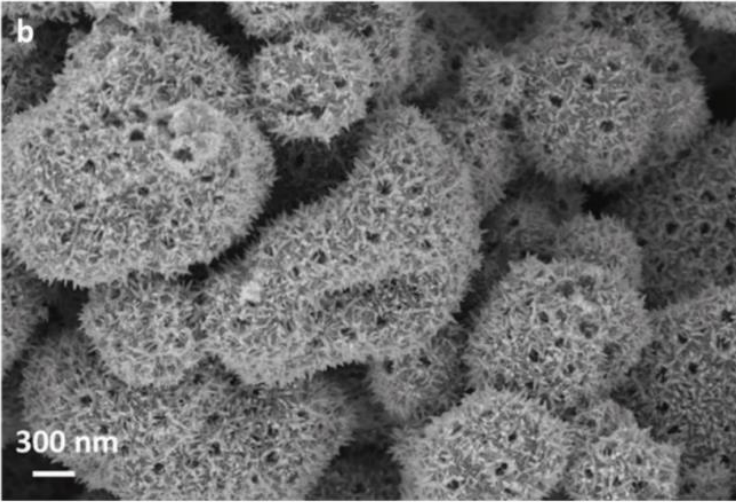
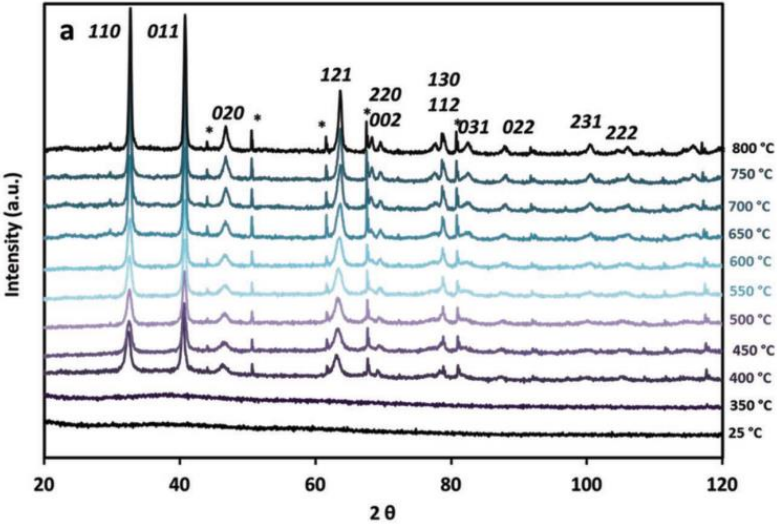
d- calcination 450 °C



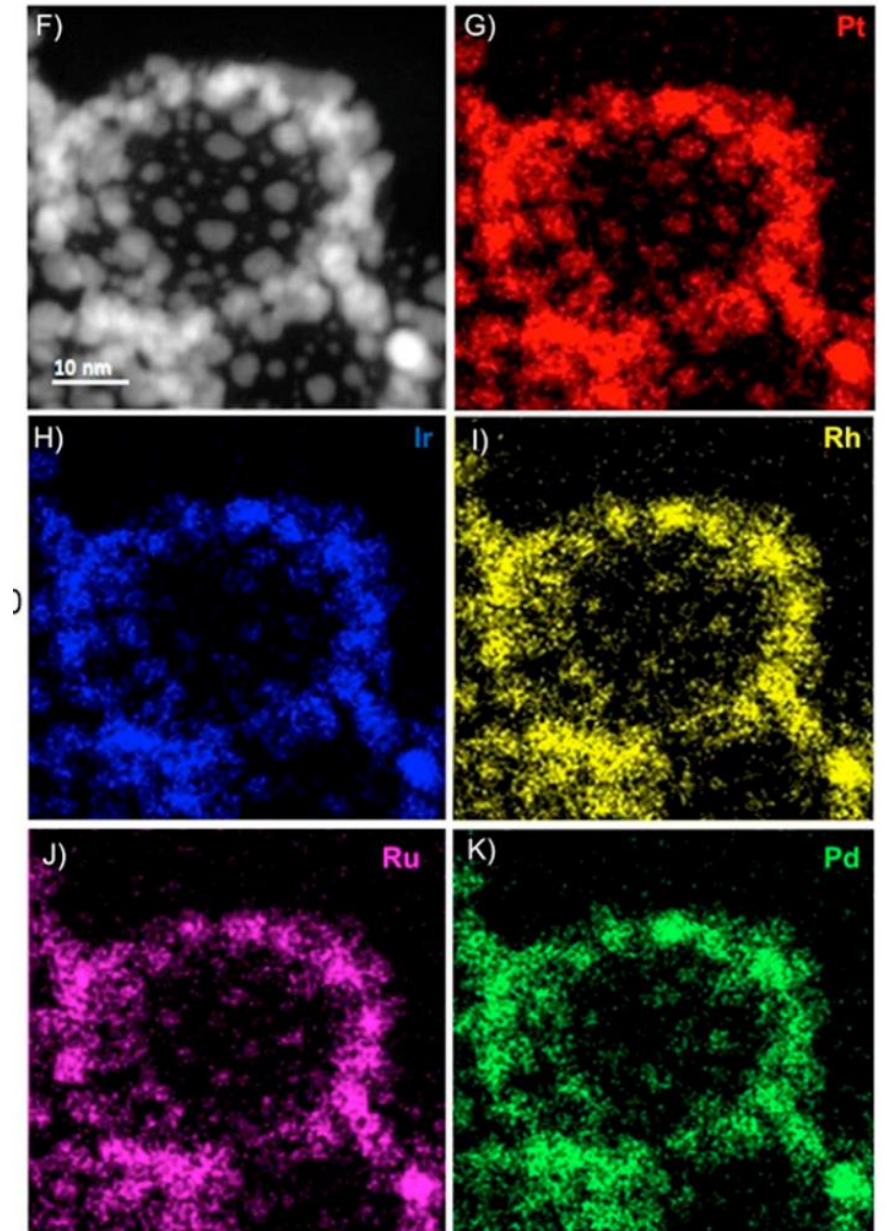
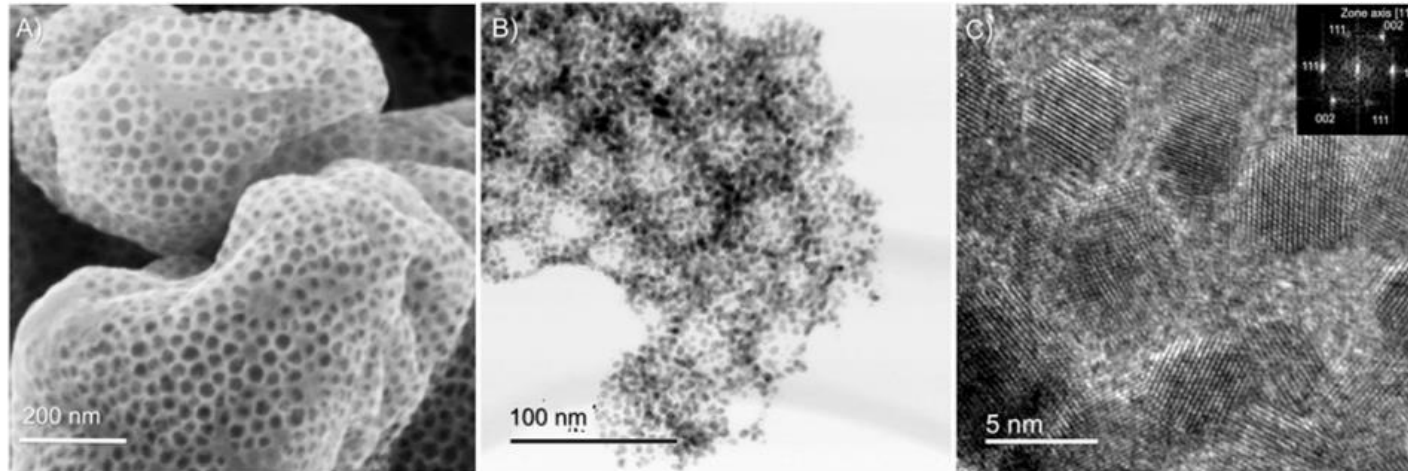
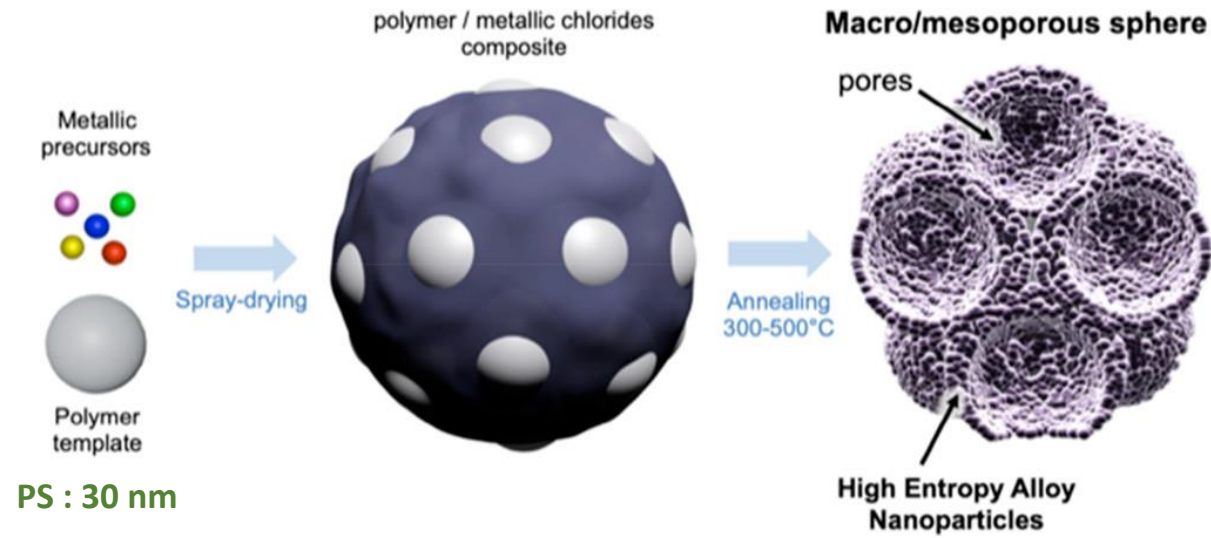
e - calcination 800 °C



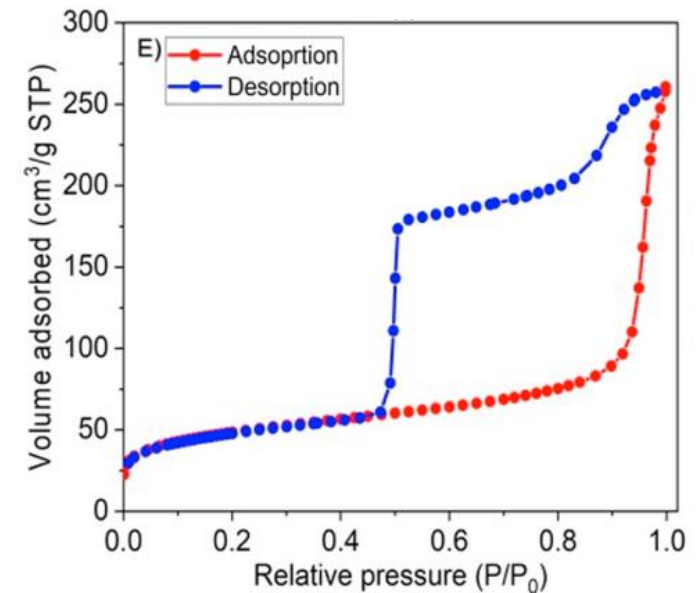
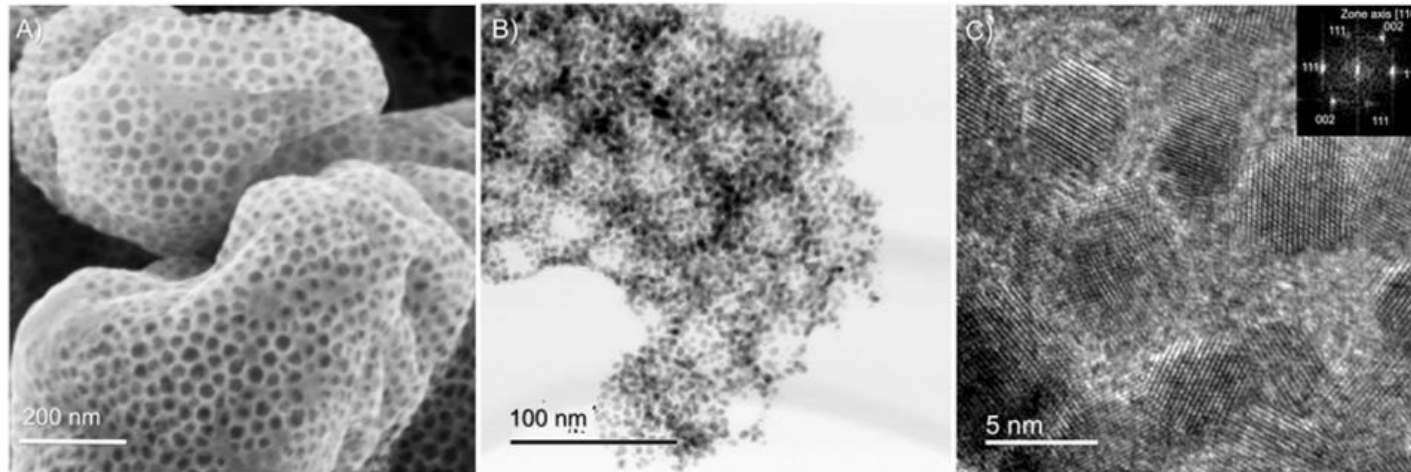
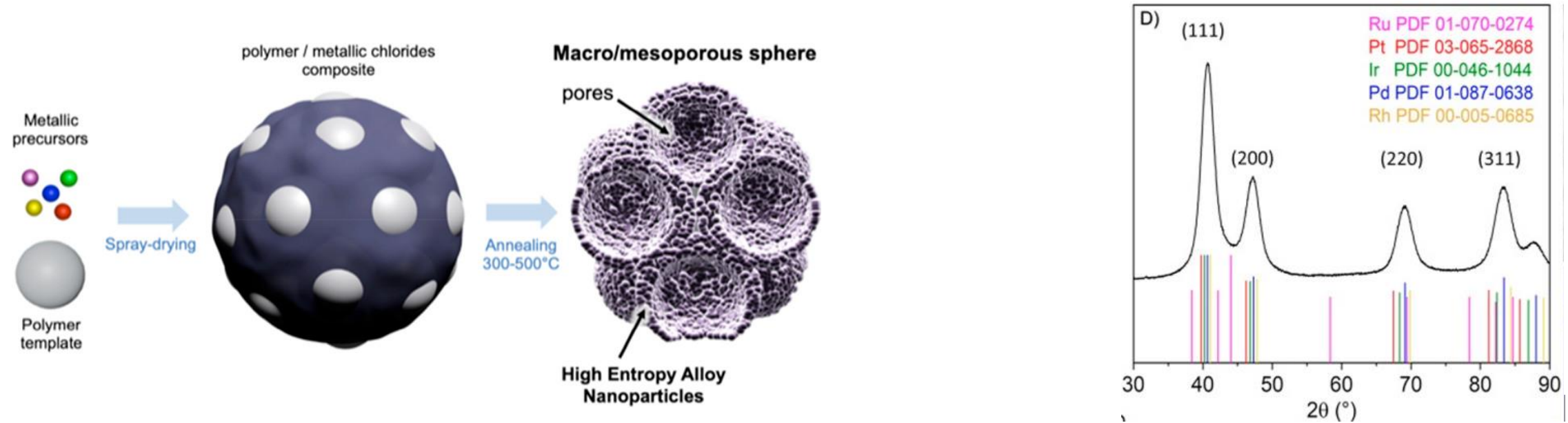
Mixed Oxides Ir_xRu_{1-x}O₂ Porous Catalysts



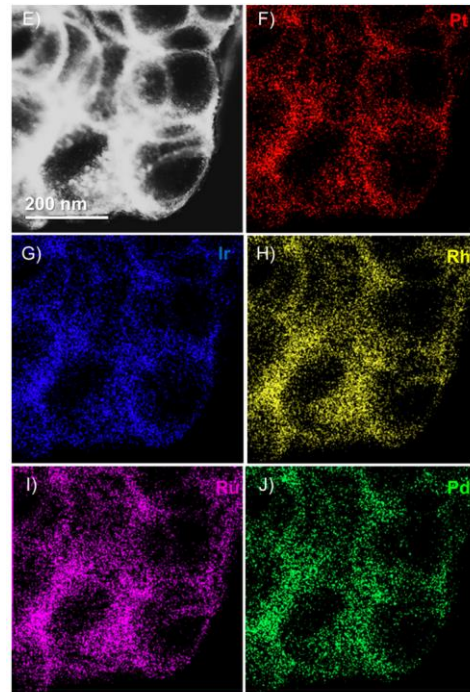
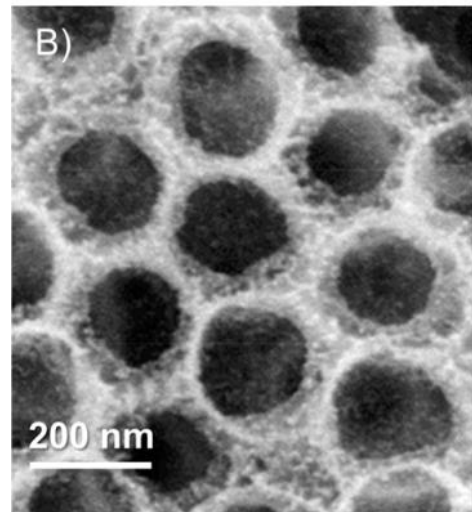
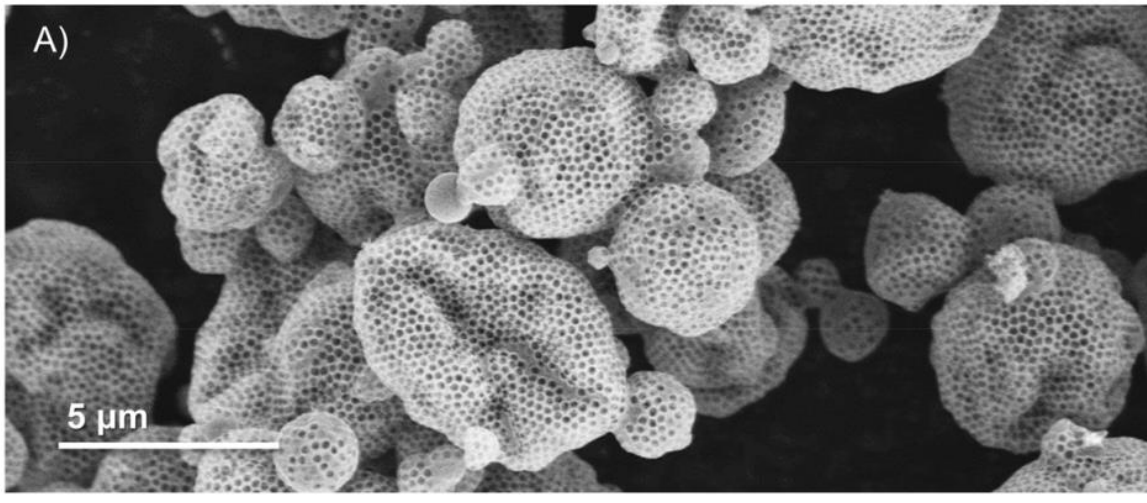
Design of Macroporous Sphere of High Entropy Alloy (HEA)



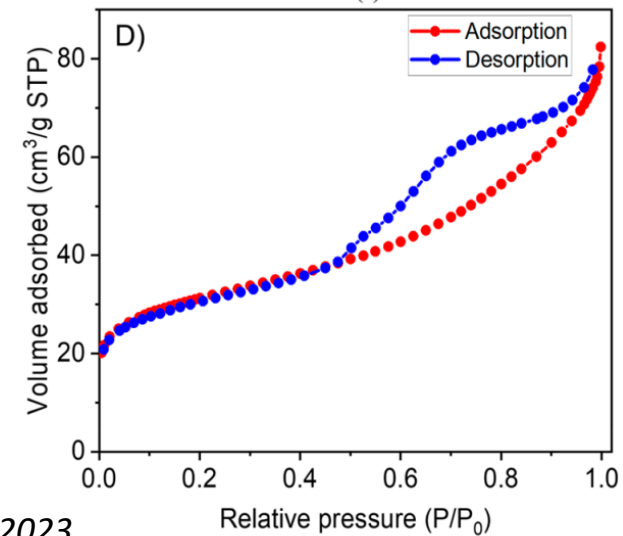
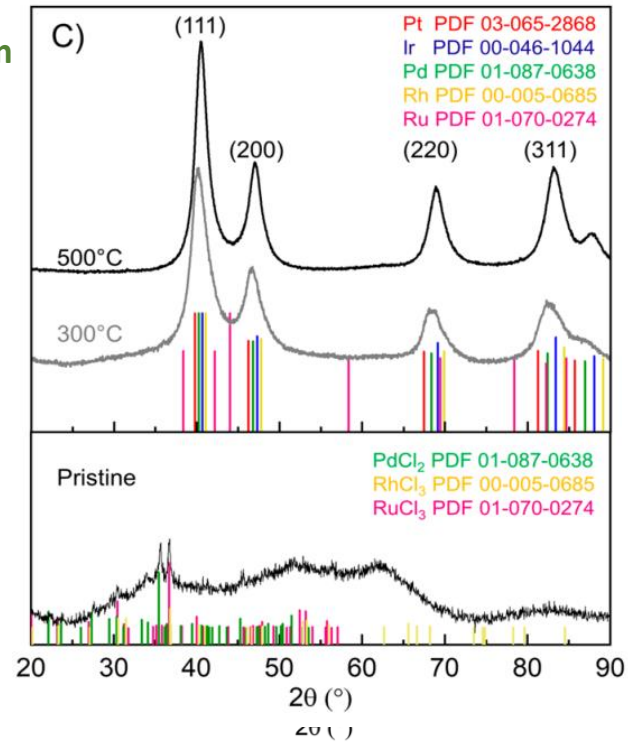
Design of Macroporous Sphere of HEA



Design of Macroporous Sphere of HEA



PMMA : 300 nm



Integrative Approaches & Materials Processing

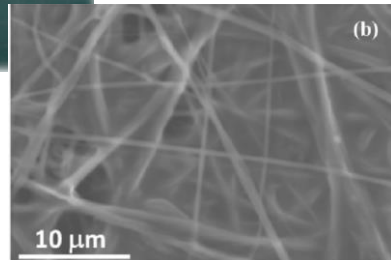
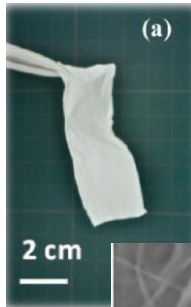
Casting

Monoliths, Foams

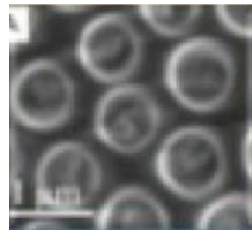


Electrospinning

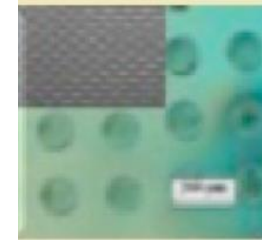
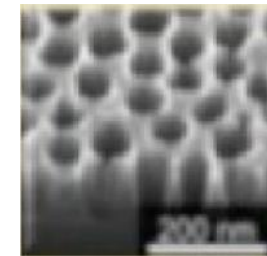
Fibers, Membranes



Dip-, spin-, spray-coating
Films, Patterns, Membranes



Soft/Hard lithography
Patterns



Spray-drying
Particles

