(co)precipitation of (hyd)roxides nanoparticles and nanostructured particles in aqueous solutions

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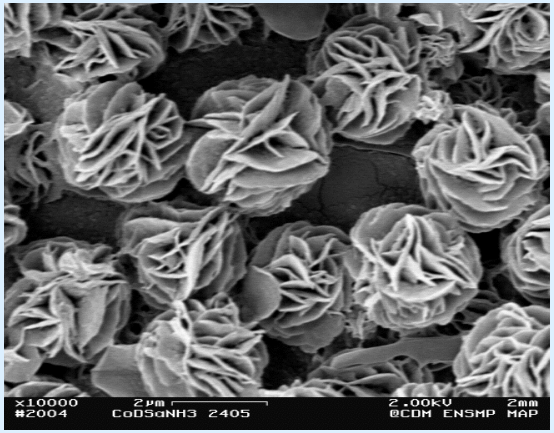
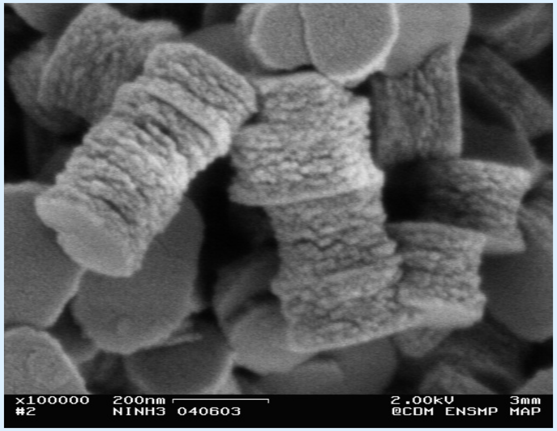
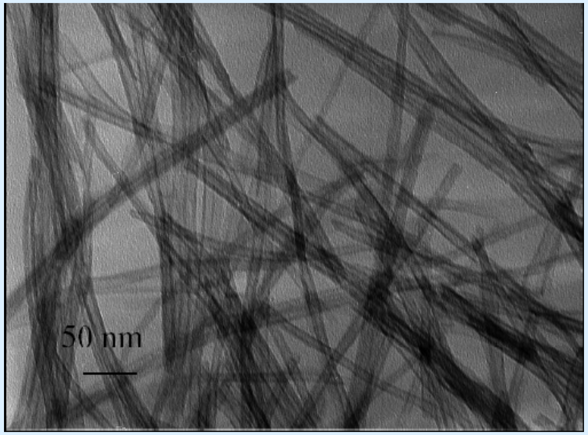






MINES-PARISTECH

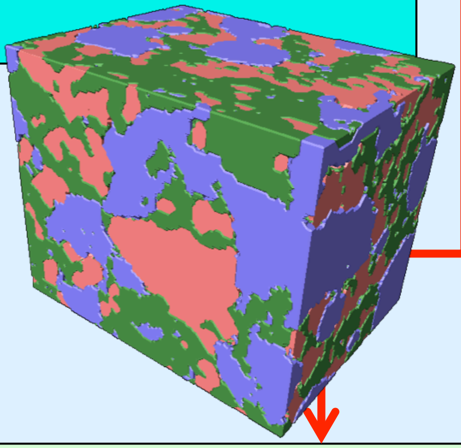
- 600 permanent staff
- 1000 students
- 20 research centers

Center for materials studies: mechanics, coatings, functional materials

Team Surfaces – Interfaces – Processes

Elaboration: materials / objects,
ceramics, metals, composites
control of their physical properties

- *Study of fundamental mechanisms*
- *Control of microstructures*
- *Control of processes*



7 researchers
5 technicians

Meeting industrial needs

- *Combining materials with antagonists properties*
- *New morphologies out of reach by classical processes*
- *New functional properties*

Processes: particles, coatings, films, fibers...

Cold spray

Screen Printing

liquid-phase syntheses

Plasma Spraying

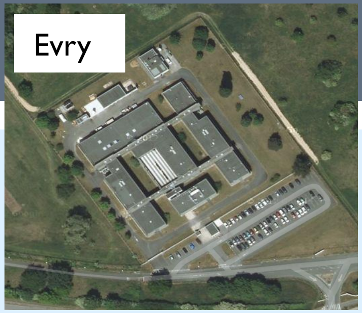
Bar Coating

composite films

LIQUID-PHASE SYNTHESES

ENSTA ParisTech

Unité Chimie et Procédés

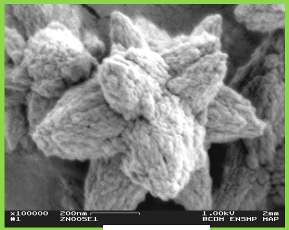


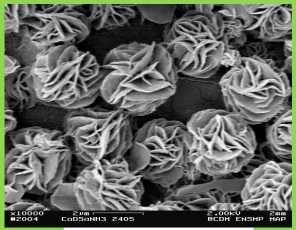
MINES ParisTech

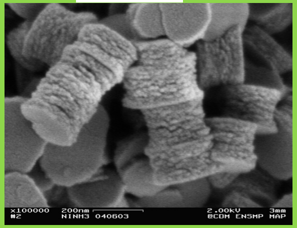
Centre des Matériaux

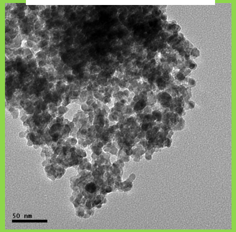
Activities: Synthesis of submicronic particles, nanoparticules and nanostructured materials by precipitation in liquid phase (mainly aqueous solutions).

Objectives: particle size, shape, composition, structure control to tune/optimize their physical properties.

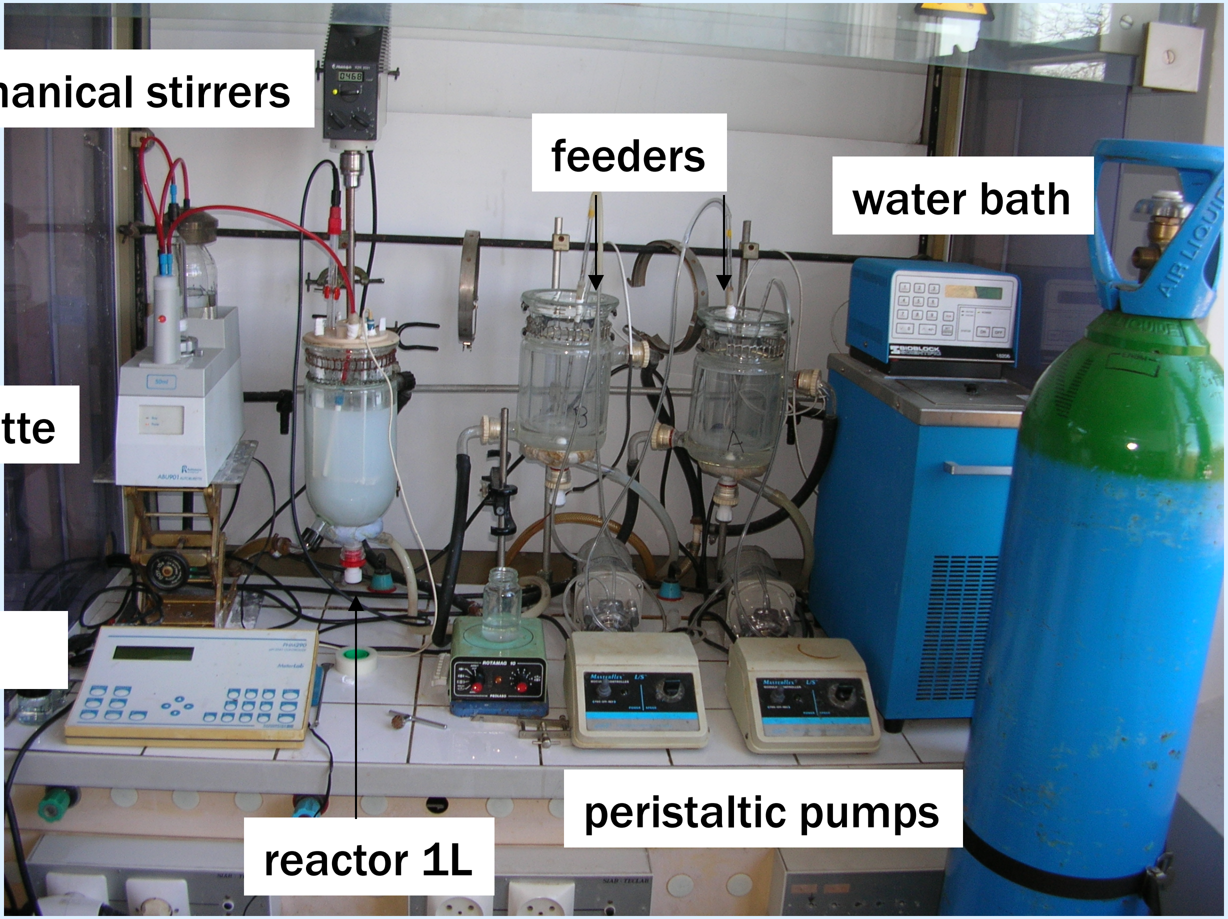

ZnO


$Co(OH)_2$


$Ni(OH)_2$


$Ti_xSn_{1-x}O_2$

Precipitation reactors



mechanical stirrers

feeders

water bath

automatic burette

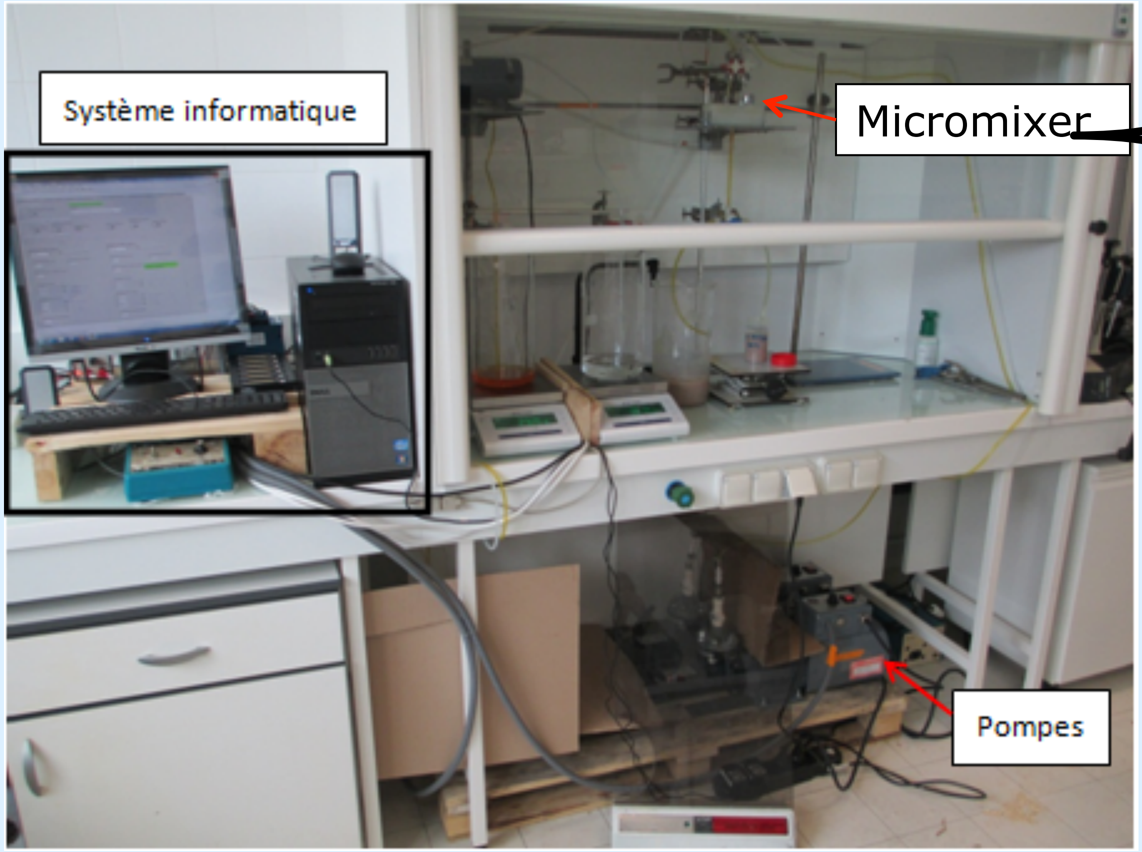
pH-stat

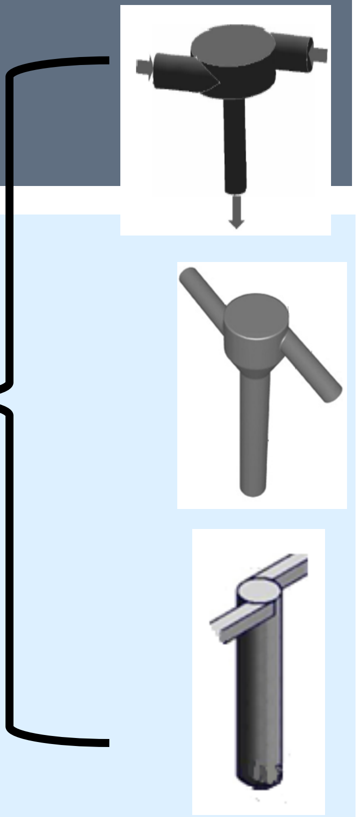
peristaltic pumps

reactor 1L

micromixers – continuous precipitation

rapid mixing





hydrothermal syntheses or ripening

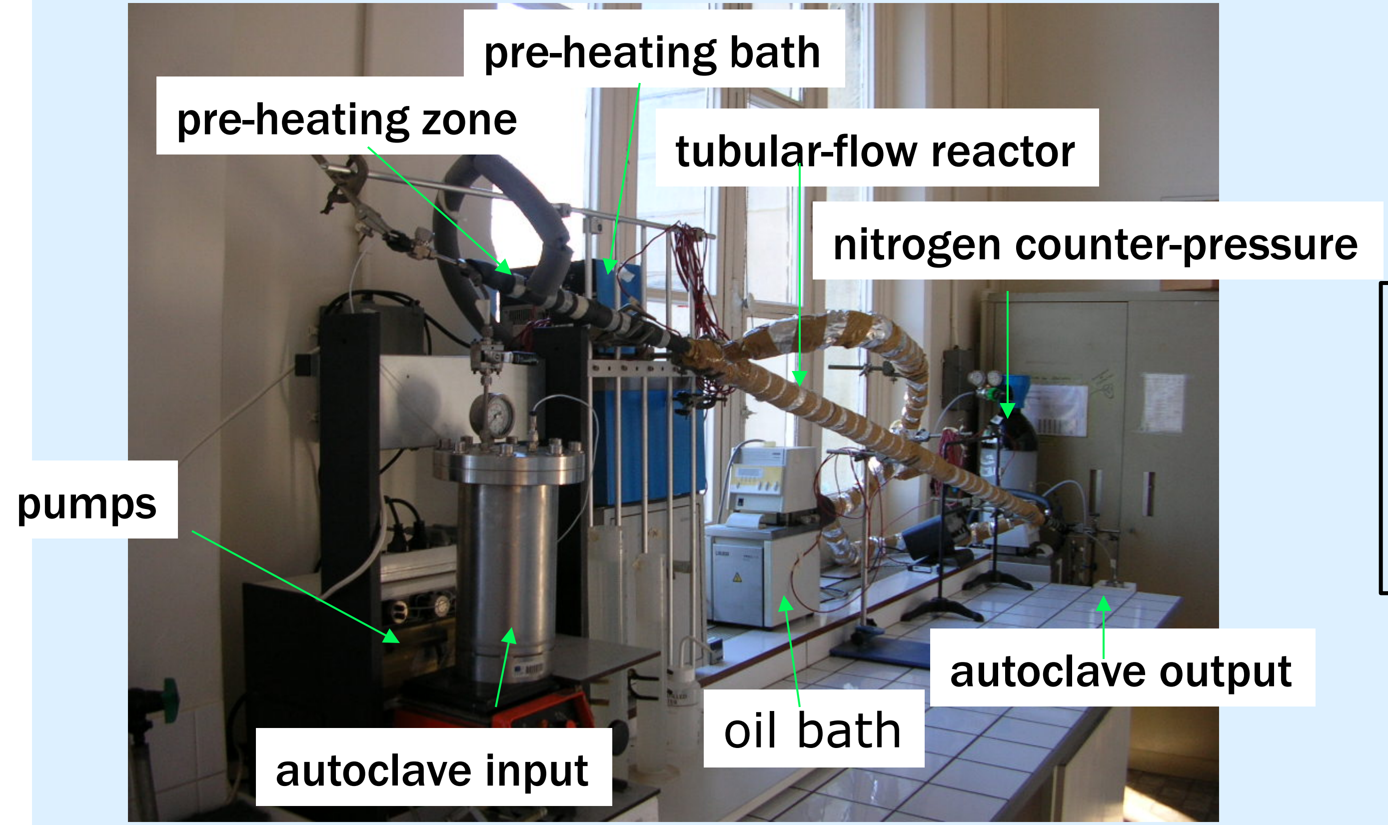
autoclaves

microwaves

Traditional heating by walls or microwave irradiation

Tubular-flow reactor

ripening – homogenous precipitation



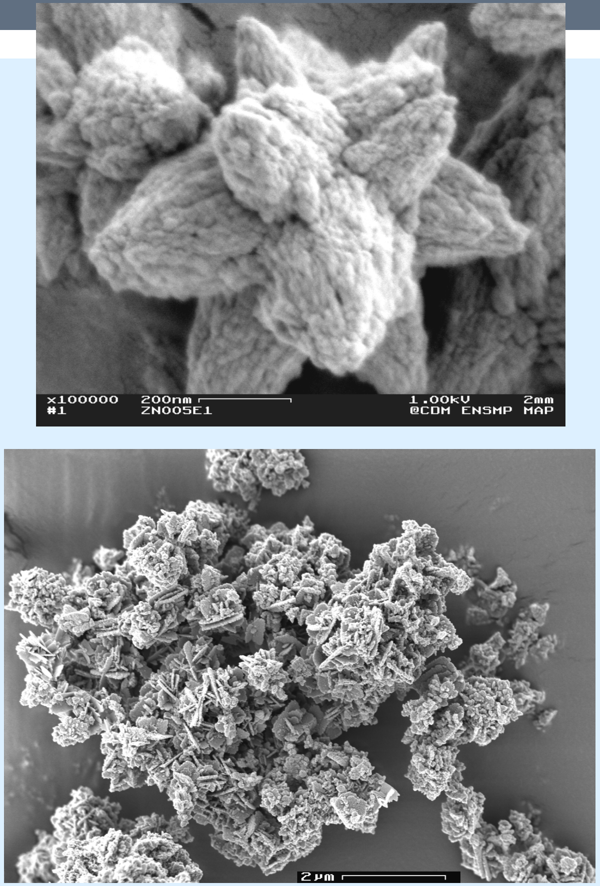
semi-continuous process with traditional heating by walls (jacketed tube)

Morphological control by the choice of the process

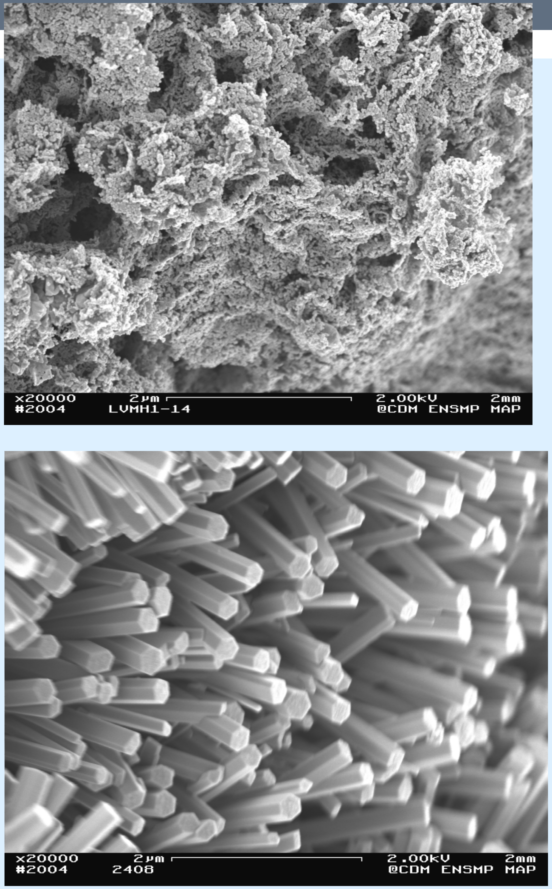
Example: ZnO

pH-induced shapes

Impact on optical properties (absorption, photoactivity...)



double jet precipitation



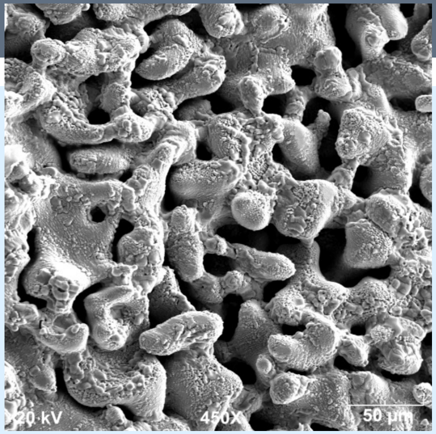
ammonia decomplexation

Coprecipitated particles as precursors for ceramics

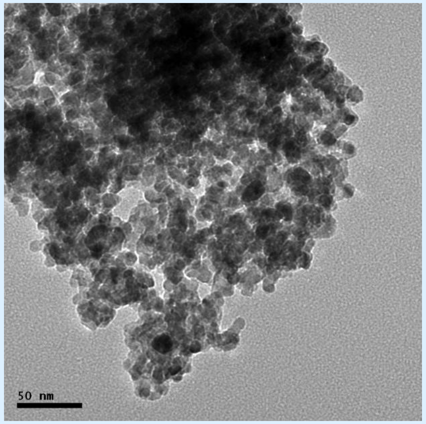
commercial
powders TiO2 and
SnO2 - mixture

annealing
1650°C

poor co-annealing

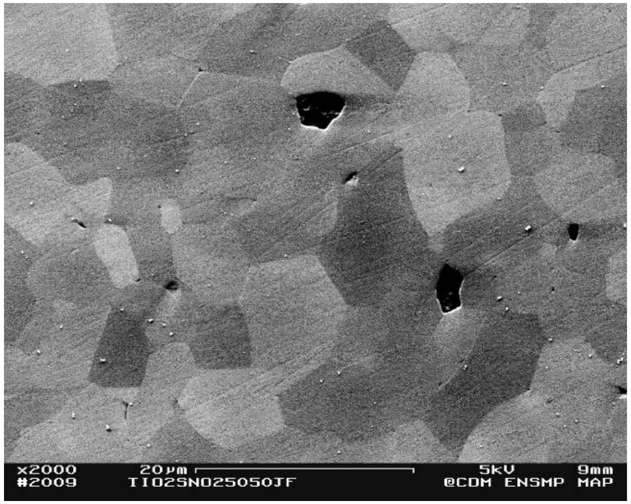


$Ti_{0.5}Sn_{0.5}O_2$ coprecipitated

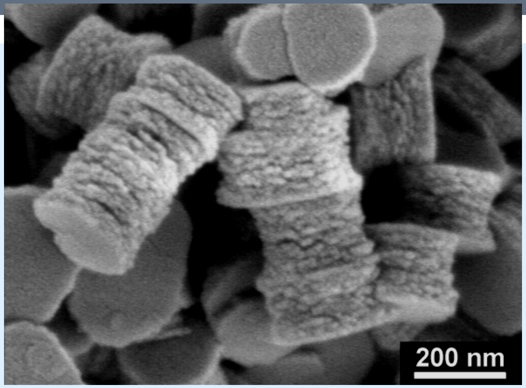


annealing
1500°C

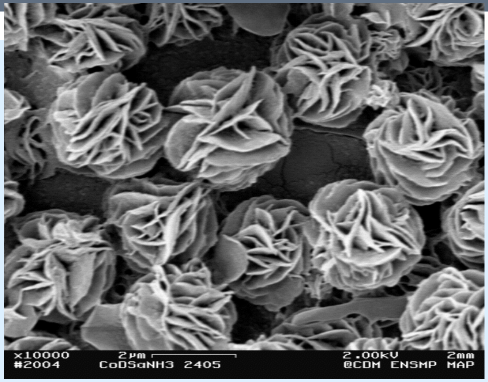
dense ceramics



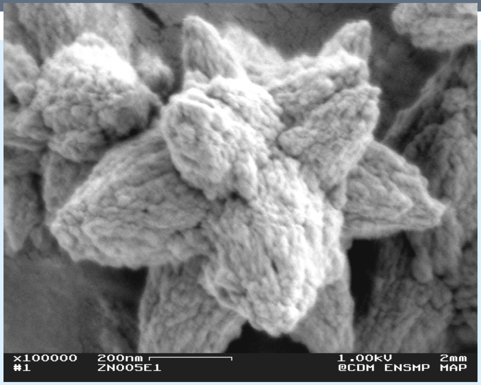
Gallery



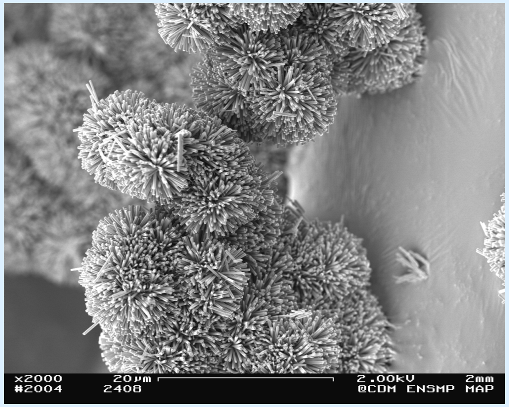
$Ni(OH)_2$



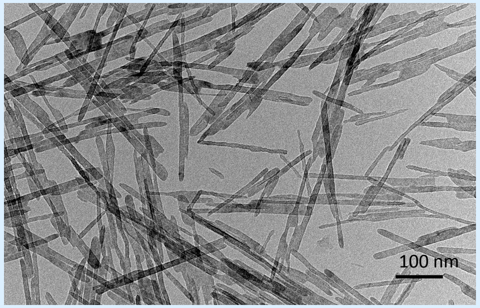
$Co(OH)_2$



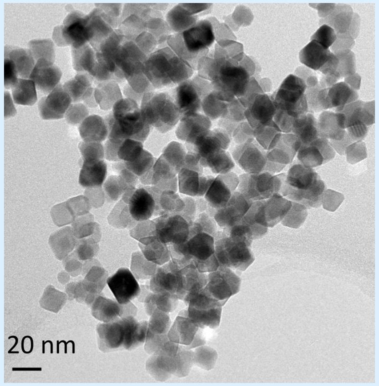
ZnO



ZnO



AlOOH



CeO_2

Outline

1) Basic concepts

2) Strategies
- Homogeneous precipitation
- double jet with pH control
- Crystallization of amorphous precipitate

3) conclusions

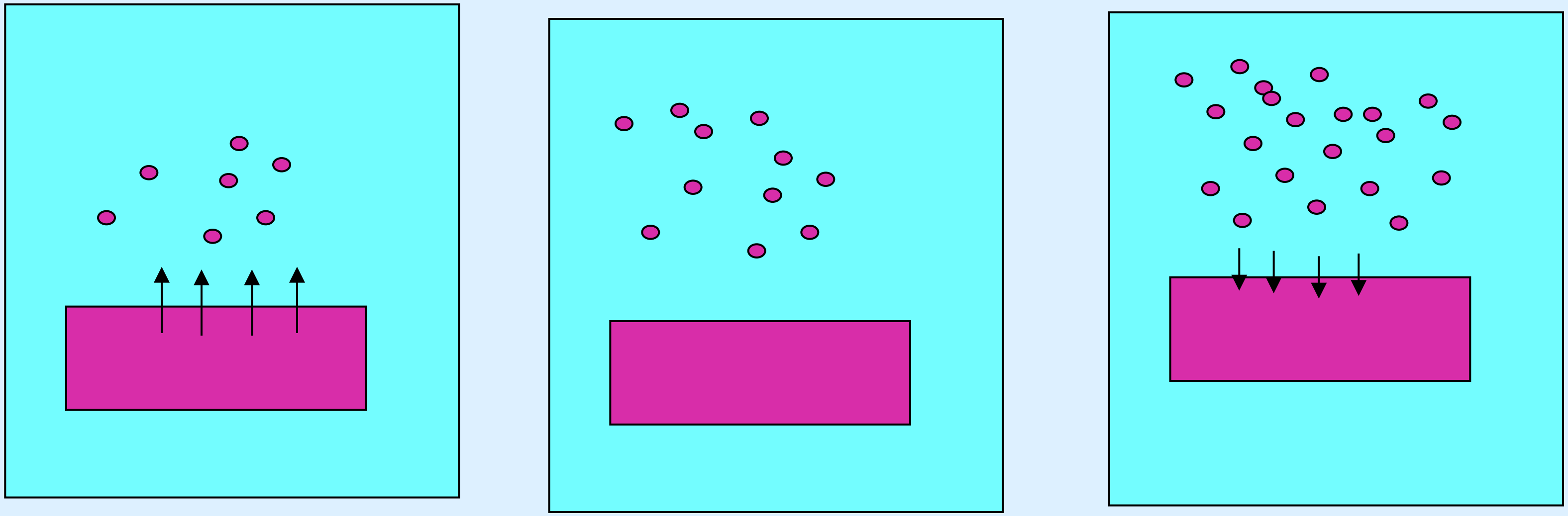
(hydr)oxide precipitation : introduction

supersaturation

Equilibrium solid-solution $[A(solution)]=[A_{equilibrium}]$

$[A(solution)]<[A_{equilibrium}]$

$[A(solution)]>[A_{equilibrium}]$
supersaturation



dissolution

precipitation (nucléation, croissance)

kinetics

Some models give kinetics laws for nucleation and growth, functions of supersaturation and surface tension e.g. :

Nucleation rate $J = J_0 \exp\left(- \frac{\Delta G_{i*}}{RT} \right)$ with $\frac{\Delta G_{i*}}{RT} = \frac{4\Theta^3}{27(\ln S)^2}$

Θ prop. Surface tension γ

Growth rate for 2D nucleation: $V_F^{\perp} = C_1 S \exp\left(- \frac{C_2 \gamma^2}{k^2 T^2 \ln S} \right)$

Ideal case: no overlapping between nucleation and growth regimes

Classification of the behaviour of non charged MO_nH_{2n-z} species

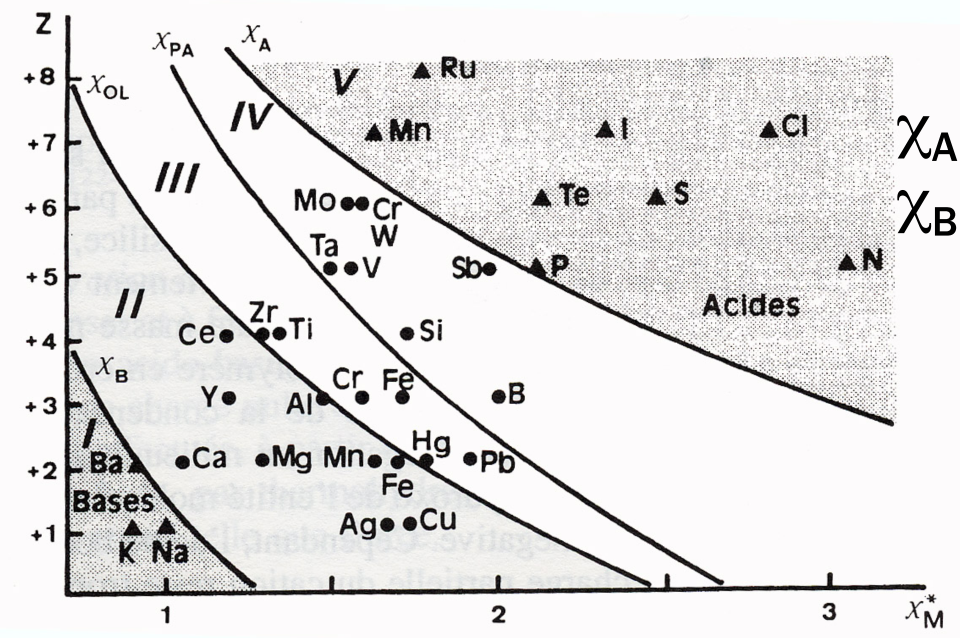


Diagram charge x electronegativity

$\chi_{A,z}$ = boundary of strong acid behaviour

$\chi_{B,z}$ = boundary of strong base behaviour

$$\boxed{xM^{z+} + yH_2O \leftrightarrow M_x(OH)_y^{(xz-y)+} + yH^+}$$

$$M(OH)_z \longrightarrow MO_{z/2}$$

Zone II: olation, hydroxides are stable

Zone III: oxyhydroxides and oxides

Zone IV: oxolation, oxides are stable

$$\boxed{M\text{-}OH + M\text{-}OH_2 \rightarrow M\text{-}OH\text{-}M + H_2O}$$

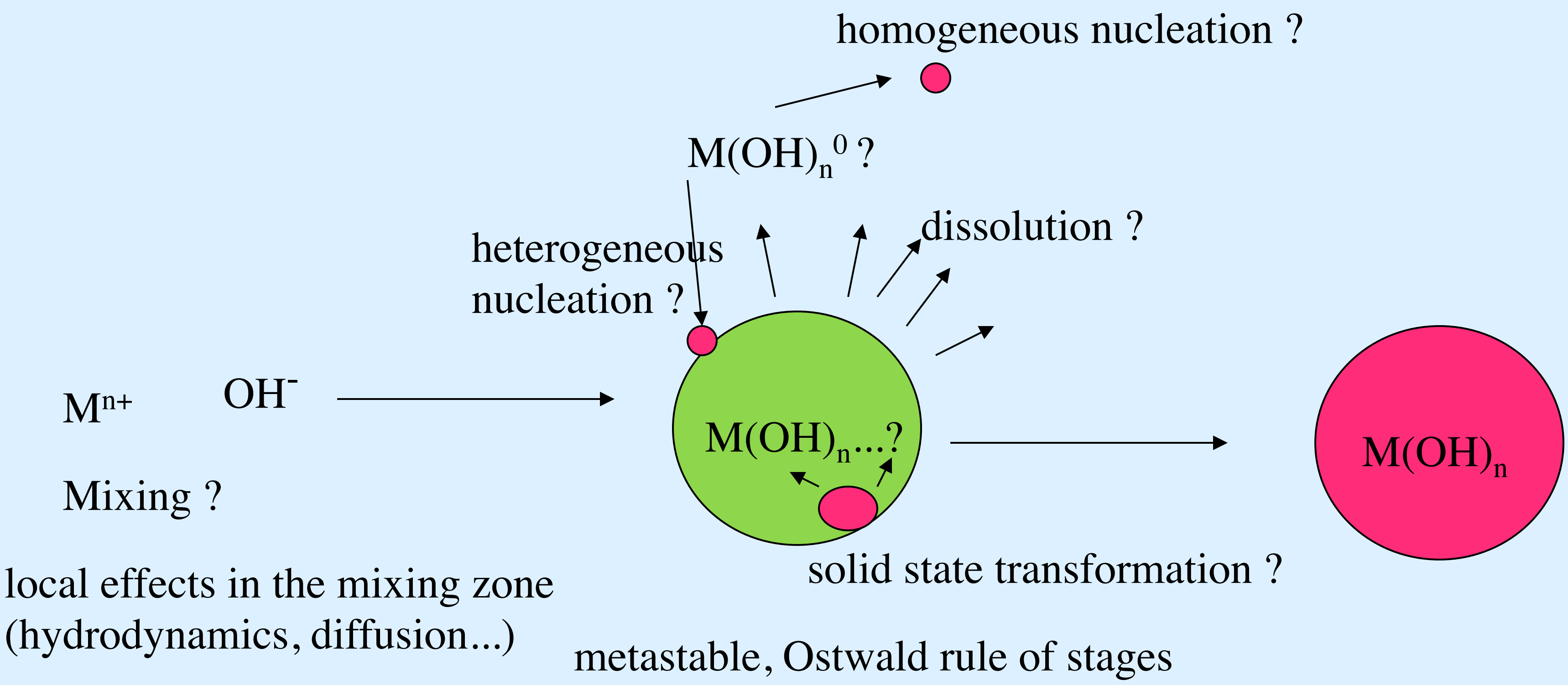
Olation

$$\boxed{M\text{-}OH + M\text{-}OH \rightarrow M\text{-}O\text{-}M + H_2O}$$

Oxolation

(JP Jolivet, de la solution à l' oxyde, CNRS Editions 1994, Fig 2.5 p47))

Hydroxides precipitation:
complex phenomena...



homogeneous nucleation ?

$M(OH)_n^0$?

heterogeneous
nucleation ?

dissolution ?

M^{n+} OH^-

Mixing ?

$M(OH)_n$...?

$M(OH)_n$

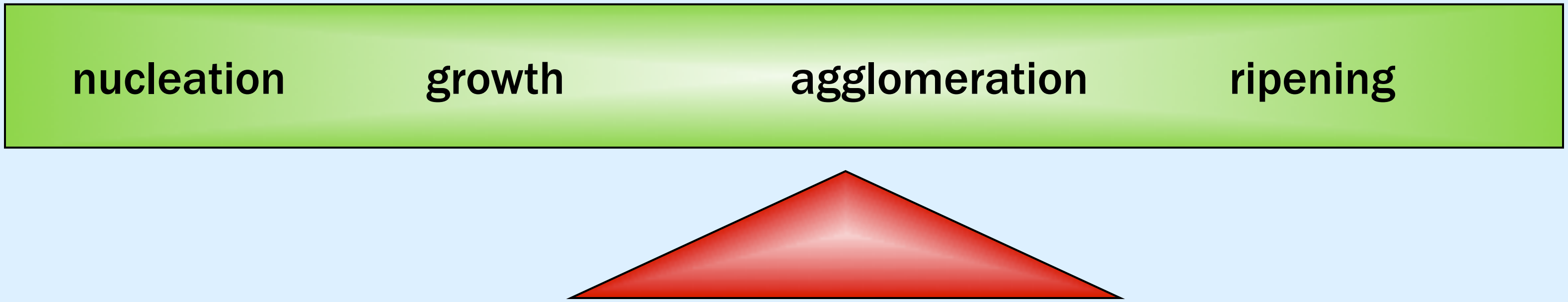
solid state transformation ?

local effects in the mixing zone
(hydrodynamics, diffusion...)

metastable, Ostwald rule of stages

The practice

Many works aiming at controlling cristallinity, size and shape of nanoparticles and multi-scale particles



nucleation **growth** **agglomeration** **ripening**

- pH
- concentration
- **hydrodynamics**
- **temperature**

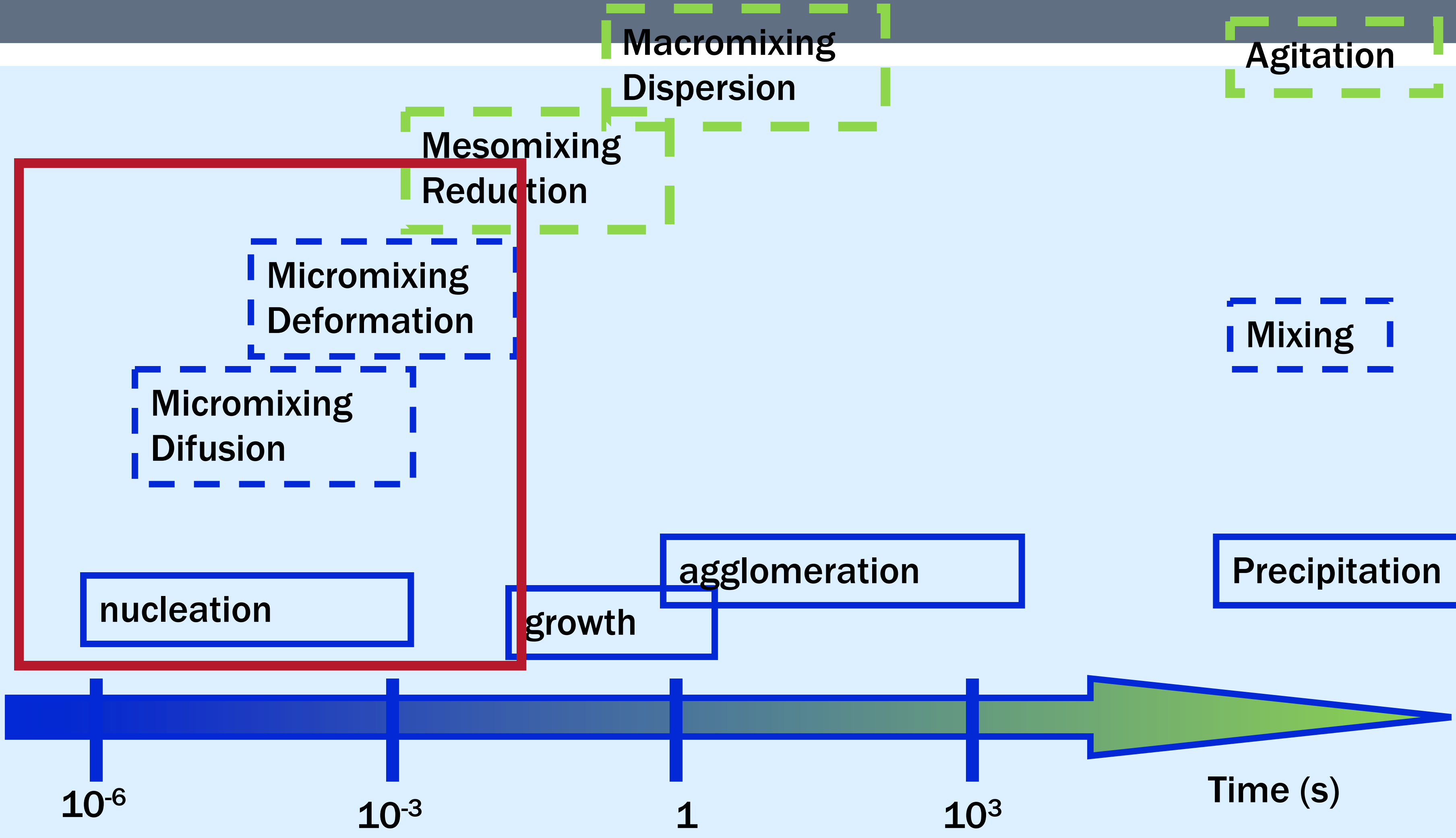
additives

- **anion**
- **surfactant**
- **polymers**
- **proteins**

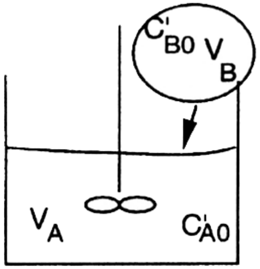
templates

- **hard**
- **soft**

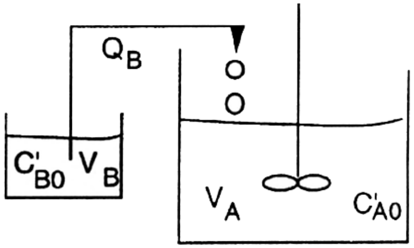
Comparation of characteristic times of mixing and precipitation processes



Reactors

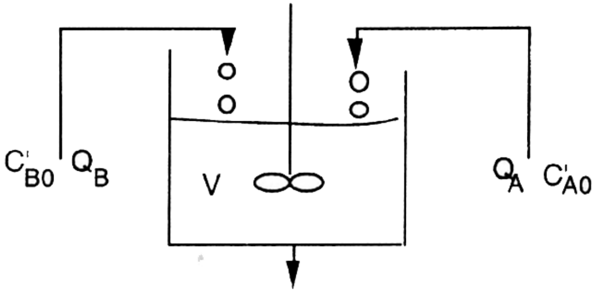


(B)



(SBSJ)

Single jet or double jet ?



(C)

Single jet:
-Nucleation close to the injection zone
- local pH ?
-pH variations in the whole volume
-Bulk pH variations with time

Double jet:
-Stationary regime
-Bulk pH control
-Nucleation and growth in the bulk

To mix or not to mix

$$M^{n+} + nOH^{-} = M(OH)_n$$

Double jet mixing

-fine control of the bulk physico-chemical conditions (pH)

-**Separated jets**: nucleation and growth in the bulk vs injection zone

-Transformation of metastable first precipitates controlled by the bulk conditions

Homogeneous precipitation

-Thermohydrolysis (acidic: Fe^{3+} or Ti^{4+})

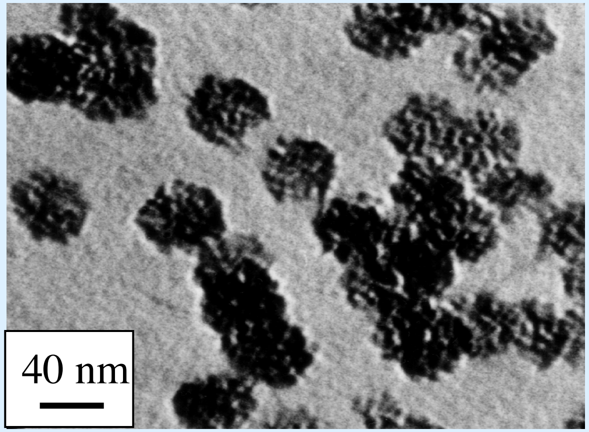
-**ammonia decomplexation** (divalent transition elements)

-In-situ OH^{-} production : urea decomposition (amorphous hydroxycarbonates)

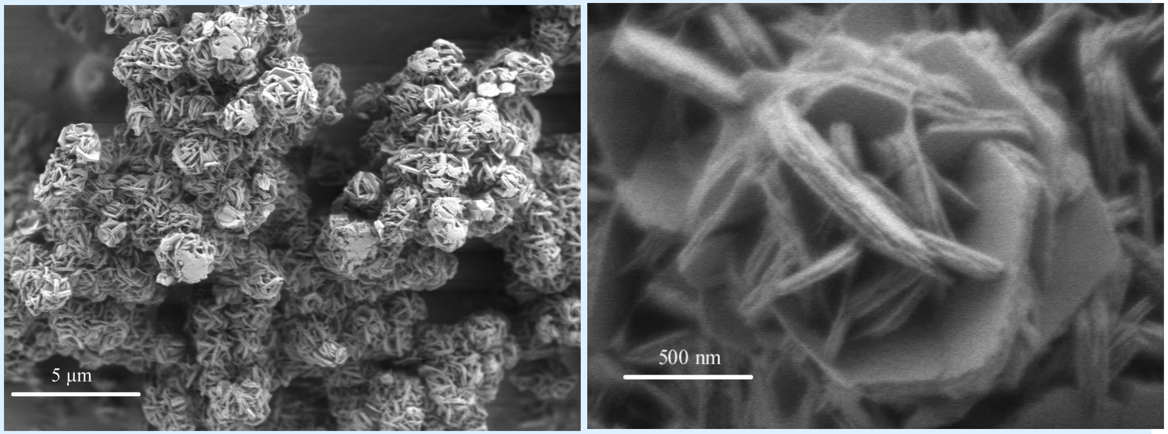
Homogeneous precipitation

Homogeneous precipitation for particle size and morphology control

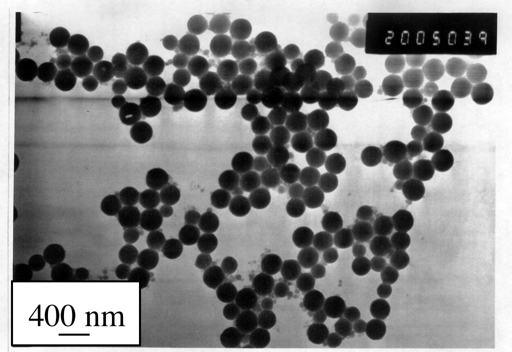
TiO_2 via thermohydrolysis:
(thesis G. Raskopf, 1990)



$Ni(OH)_2$ via heating a solution of $Ni(NH_3)_6^{2+}$
(thesis Ph. Carlach, 2003)



$Y(OH)CO_3$ via urea decomposition
(thesis S. Neveu, 1995)



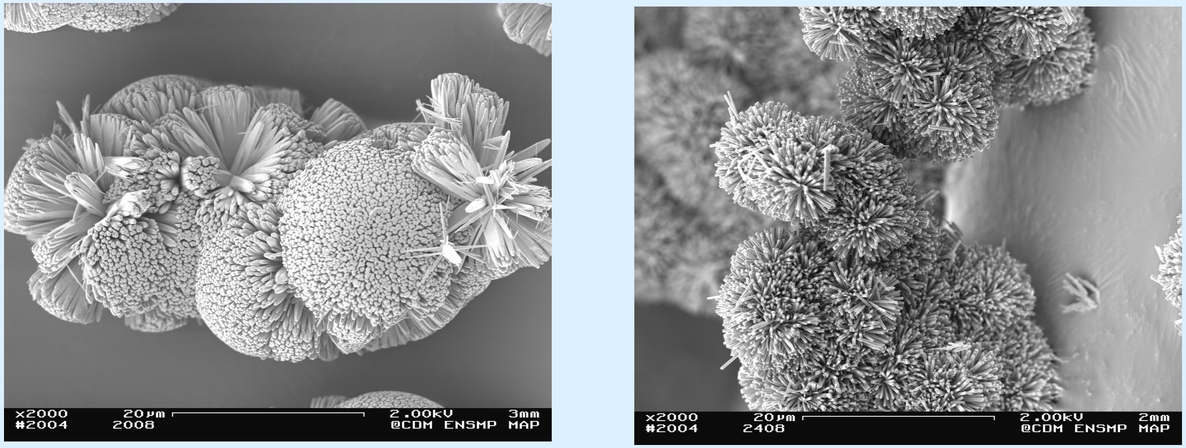
u_0=0.20 mol.dm^{-3}, y_0=0.02 mol.dm^{-3}, T=100.5 °C, $t_{préc}$=65 minutes, c_{germes}=1.27 10^{18} part.m^{-3}, N_R=600 rpm, grossissement 40000.

Homogeneous precipitation:
-monodisperse particles
-nanostructures

Homogeneous precipitation
Ammonia ligand removal

Zinc oxide pompom-like particles, shape control by pH

J.-F. Hochepied, A.P. Almeida de Oliveira, V. Guyot-Ferréol and J.-F. Tranchant, J. Crystal Growth 283 (2005) 156-162

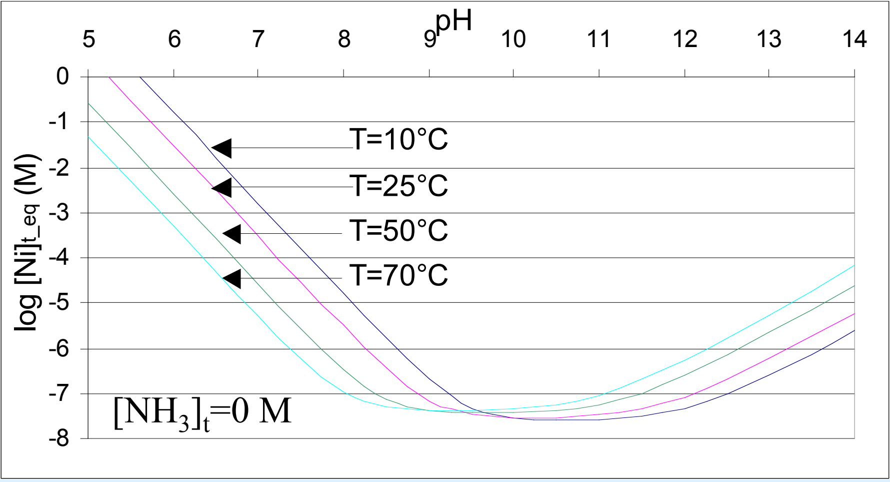


Nickel and cobalt hydroxides:: pH and surfactant effects

C. Coudun and J.-F. Hochepied, J. Phys. Chem. B 109 (2005) 6069-6074

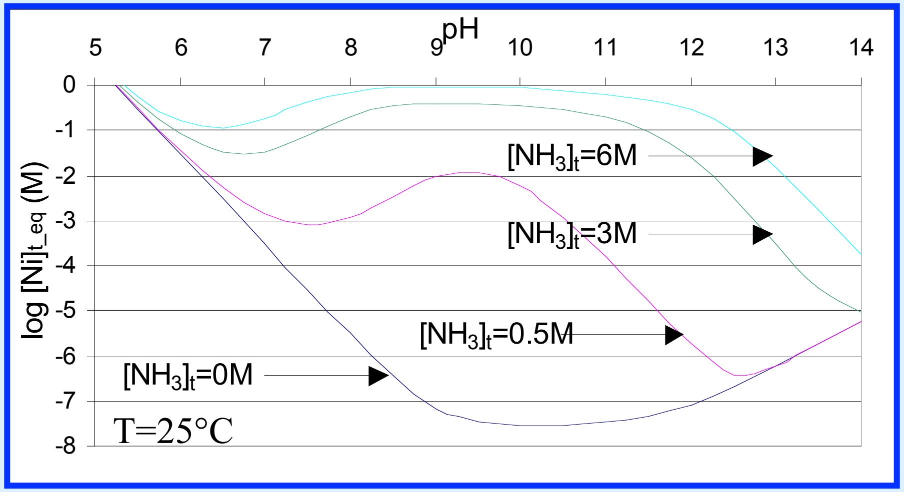
C. Coudun, E. Amblard, J. Guihaumé and J.-F. Hochepied, Catalysis Today, 124 (2007) 49-54

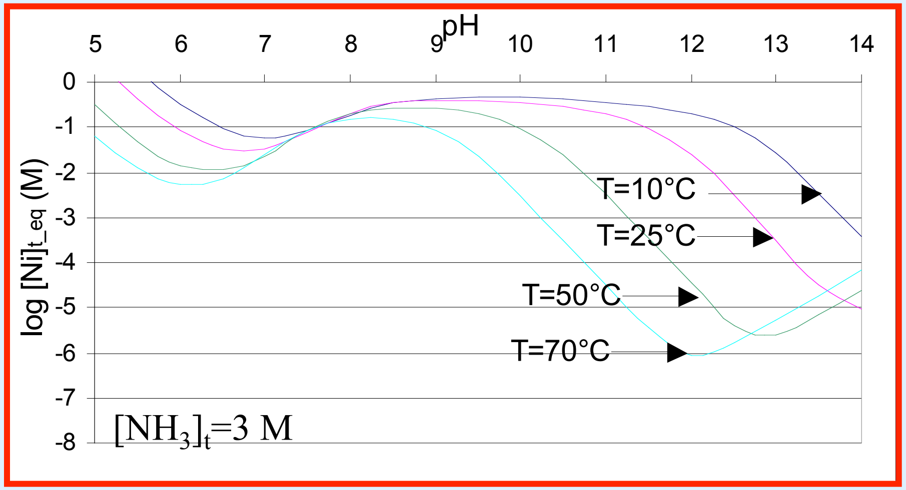
$Ni(II)-H_2O-Ni(OH)_2\downarrow\ NH_3$



NH_3:complexation =high solubility

Very sensitive to temperature



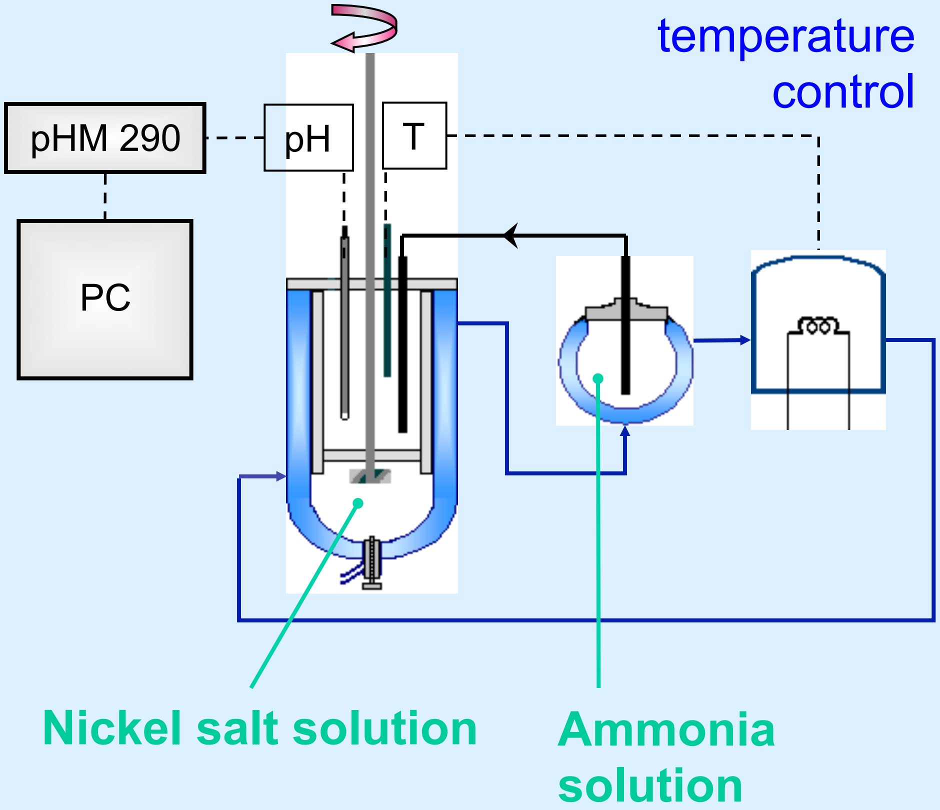


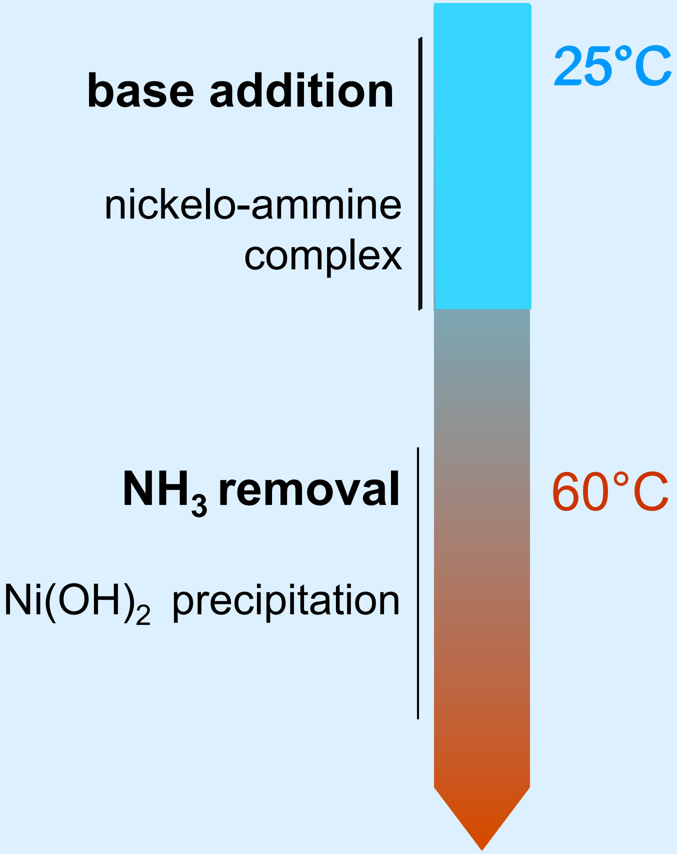
Synthesis by ammonia decomplexation

1) NH_3 slow addition to nickel salt at25°C

$$Ni^{2+} + n\,NH_3 \longrightarrow Ni(NH_3)_n^{2+}$$

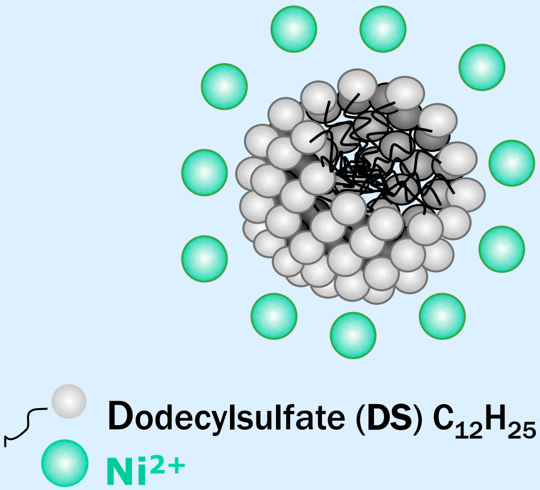
2) Heating (60°C), free pH , open air





Coupling homogenous precipitation/ surfactant

comparison: nitrate $Ni(NO_3)_2$, sulphate $NiSO_4$
and surfactant (dodecylsuphate) functionalized nickel : $Ni(DS)_2$ ($DS=C_{12}H_{25}SO_4$)



Dodecylsulfate (DS) $C_{12}H_{25}$-O-SO

Ni^{2+}

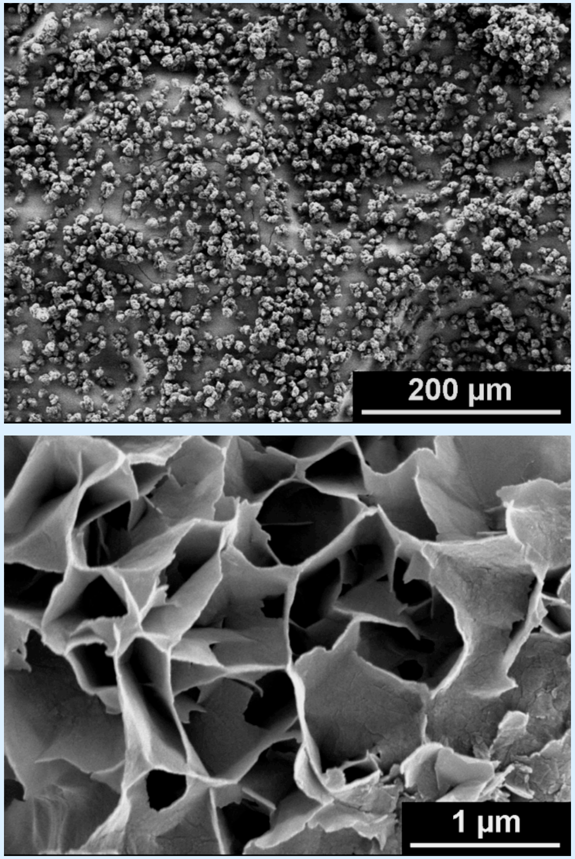
c > c.m.c.
direct micelle
~ 10 nm

Reactant: high local concentration
Contrary to nitrate or sulphate, dodecylsulfate does not enter in the hydroxide structure

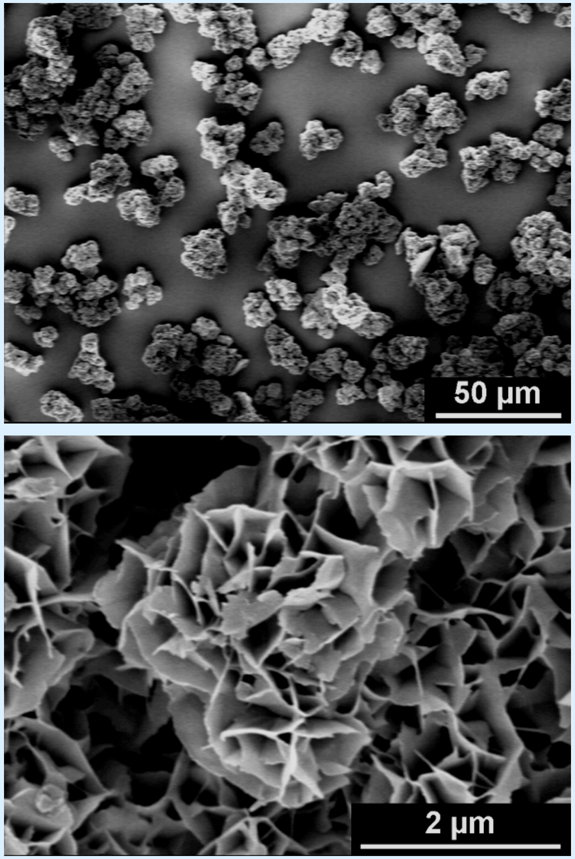
Morphologies

particles ~10 µm : sponge-like

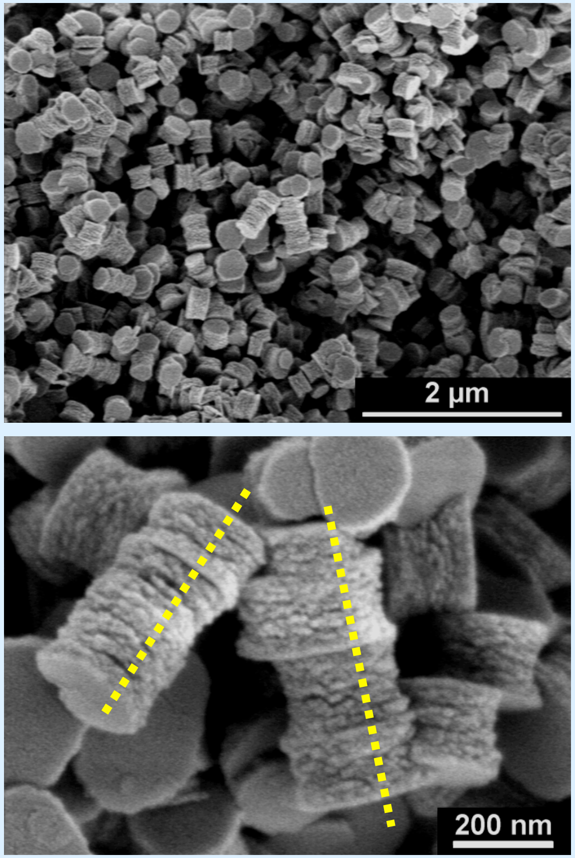
Homogeneous nano-cylinders
(300 nm x 200 nm)



$Ni(NO_3)_2$

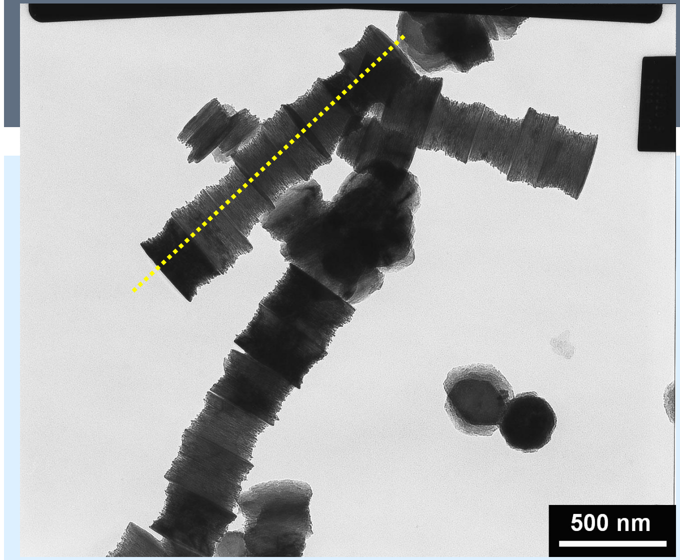


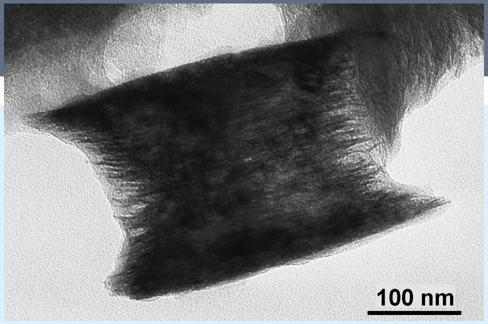
$NiSO_4$

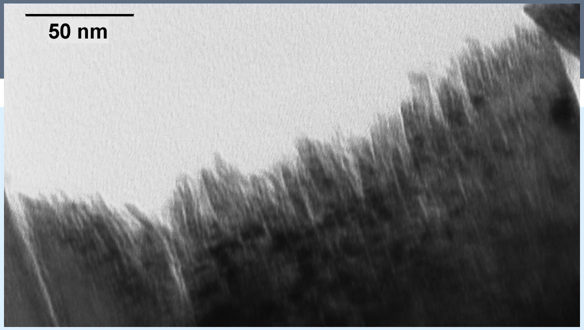


$Ni(DS)_2$

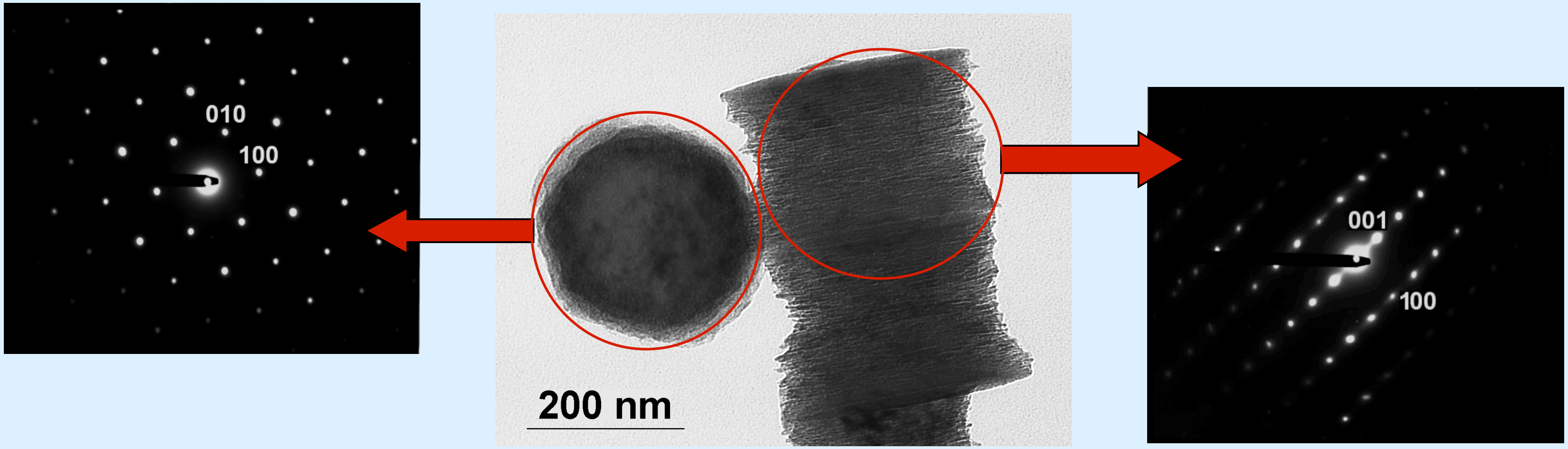
Cylinders from $Ni(DS)_2$ precursor





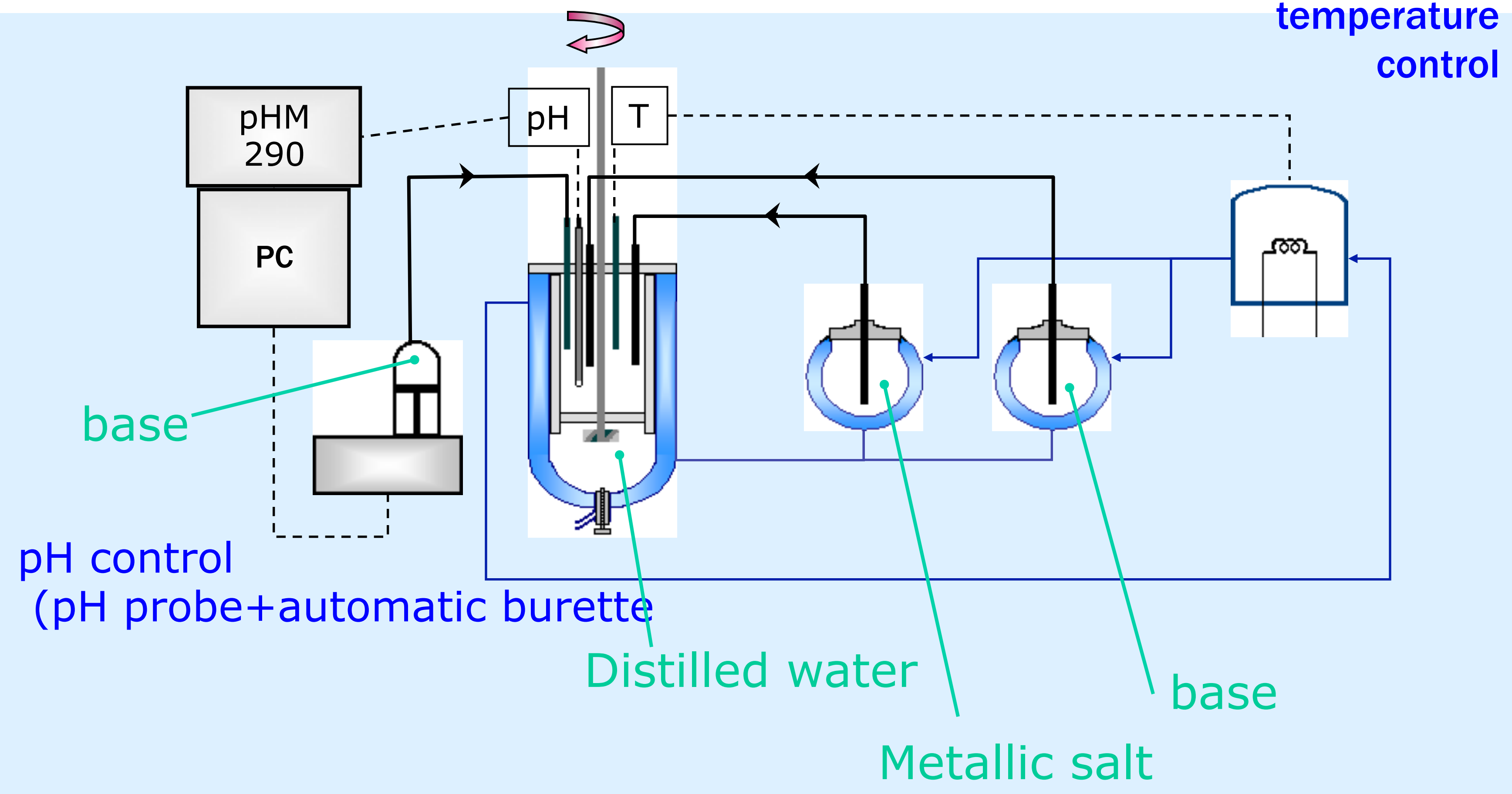


Stacks of $Ni(OH)_2$ pancakes ??

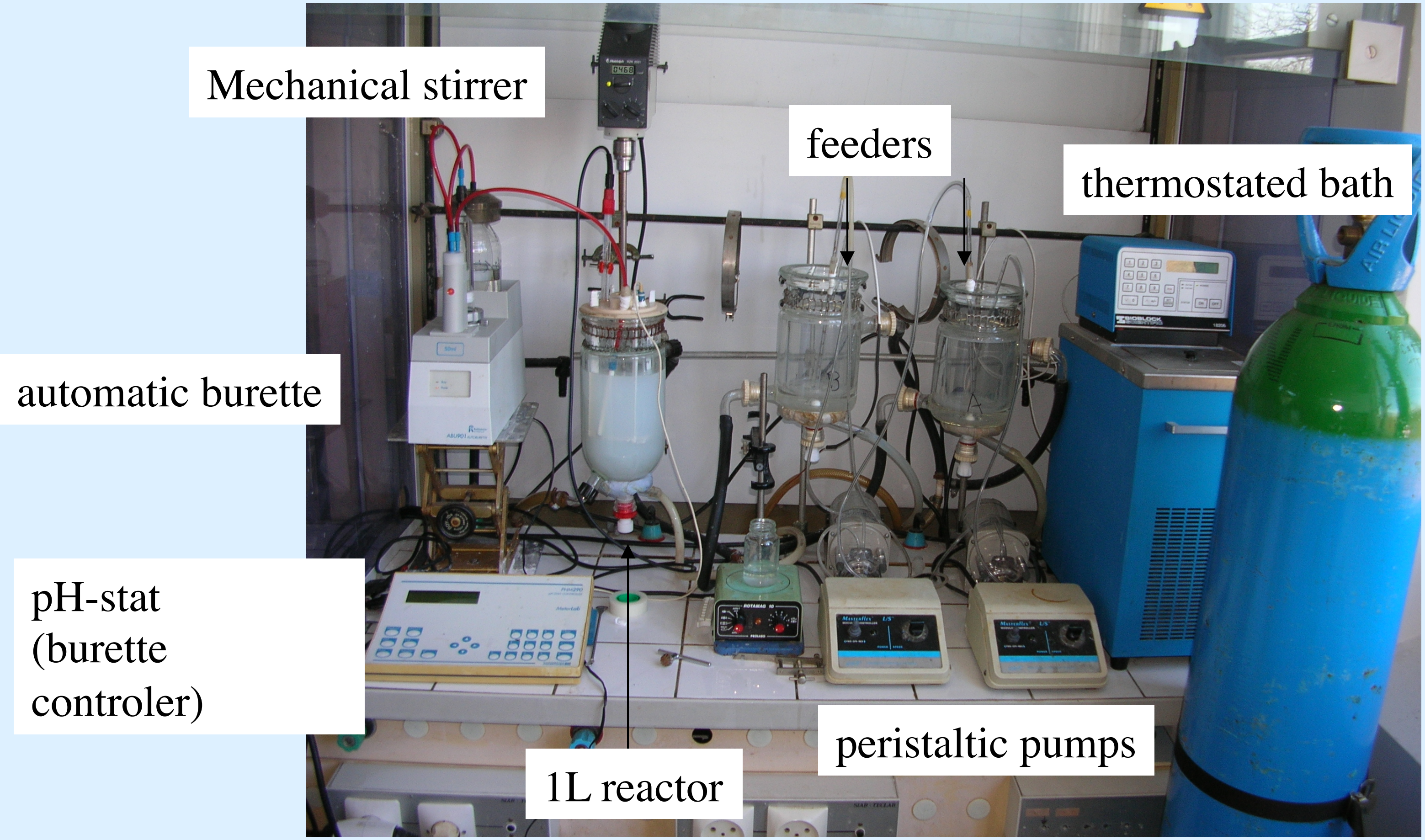


double jet

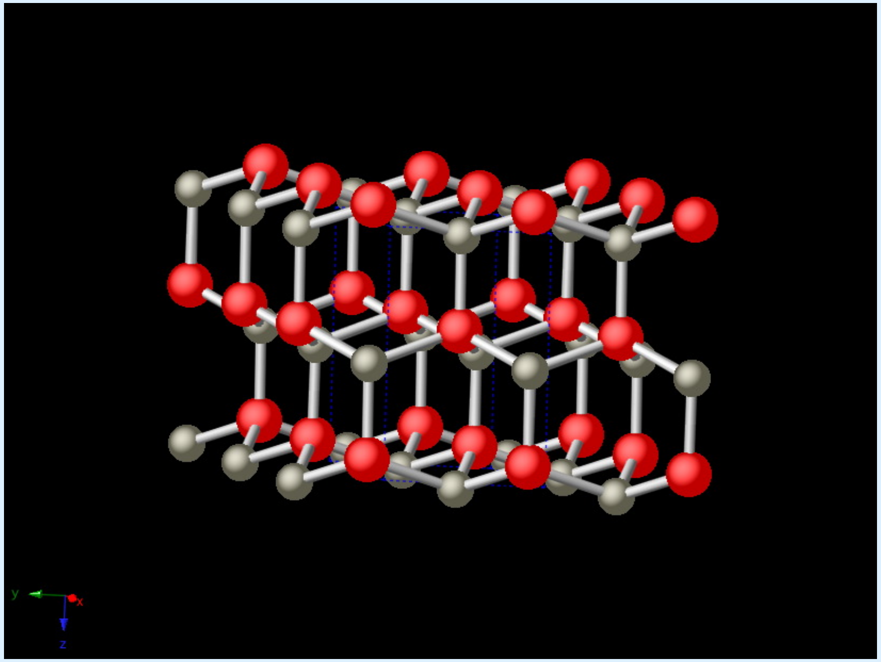
double jet with pH control



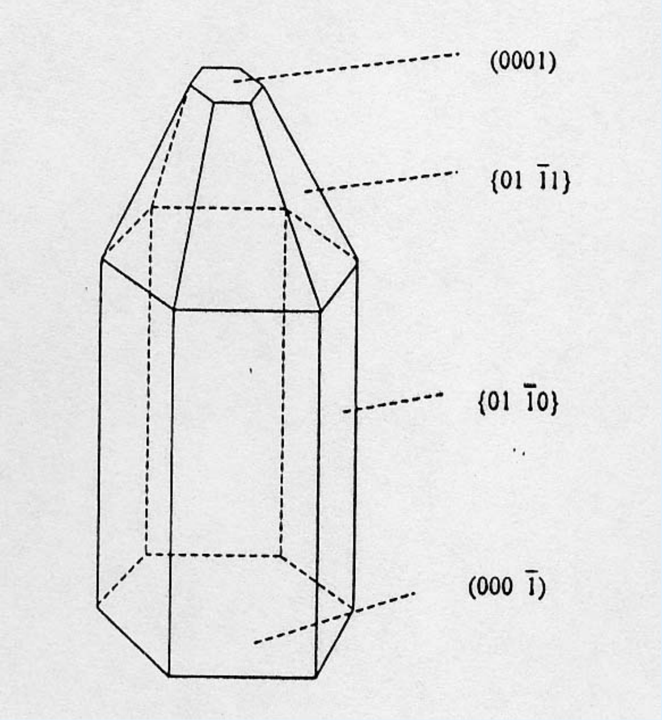
double-jet: experimental set-up



Zinc Oxide

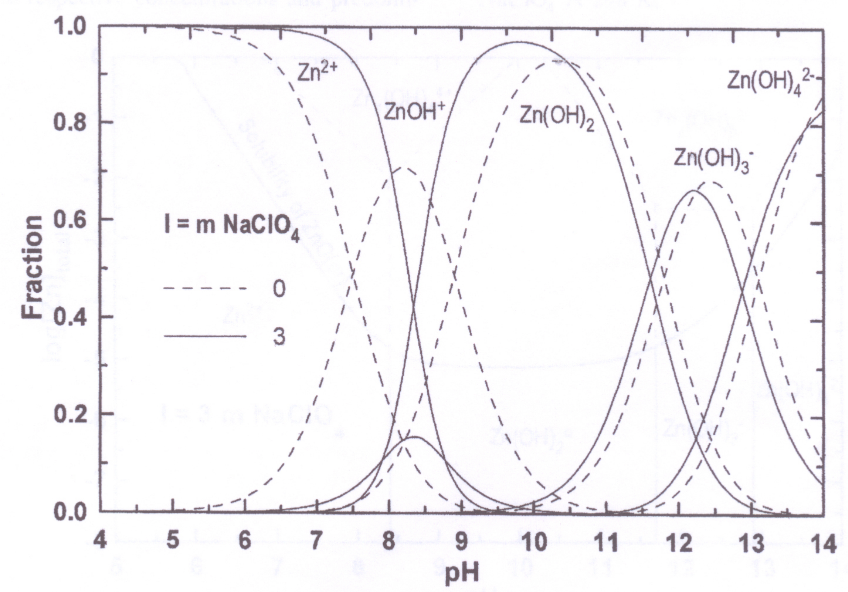


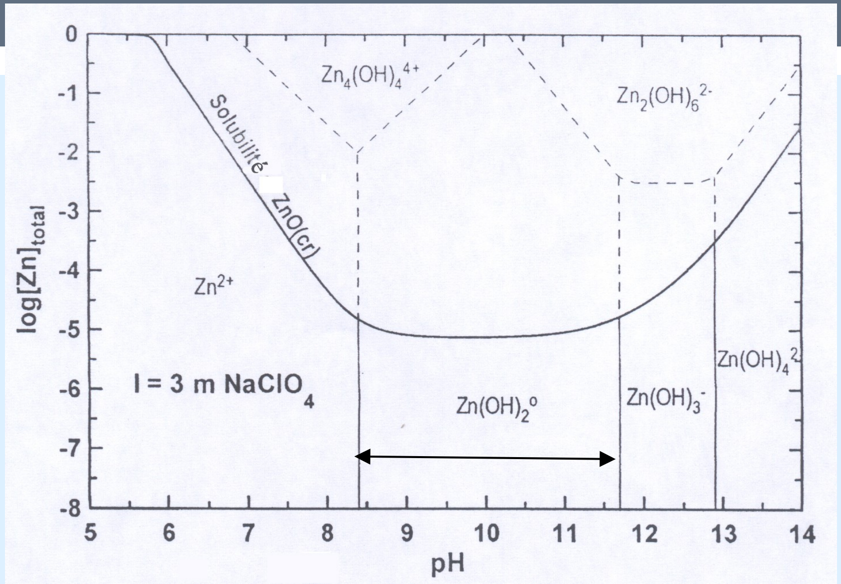
hexagonal, a=3.25 Å, c=5.21 Å



Growth habit **[LI et al., 1999]**

speciation and solubility



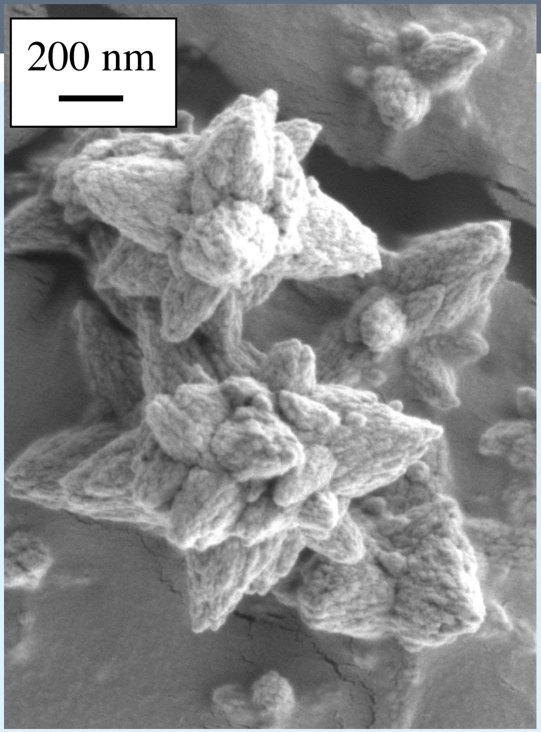


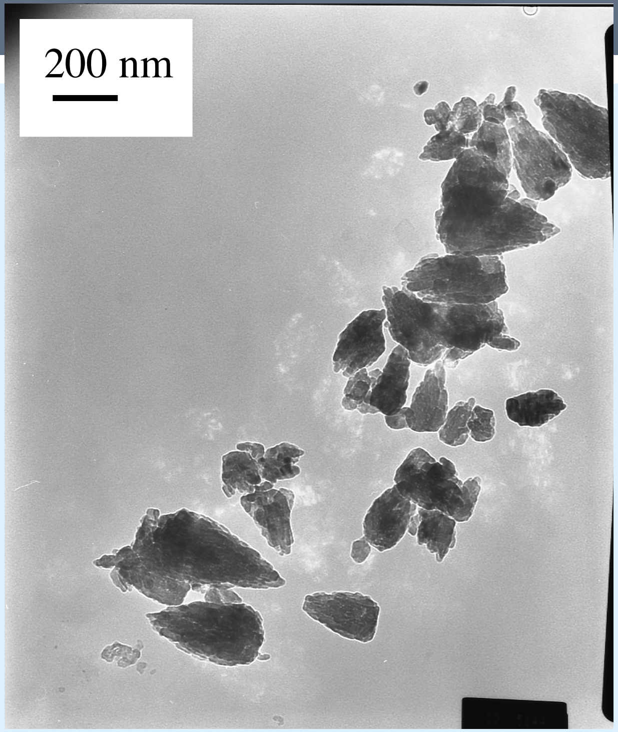
double jet: pH controled during precipitation
speciation and supersaturation fixed

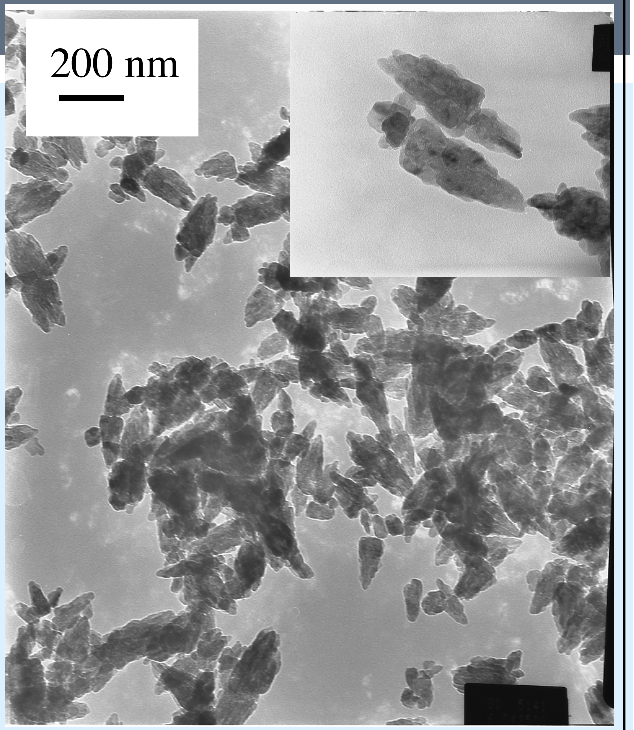
Choice of pH value: plateau of minimum solubility

plateau spreads over 3 pH units
-supersaturation
-speciation
-Particle surface charge

ZnO: Particles obtained at 25°C, pH=10.5





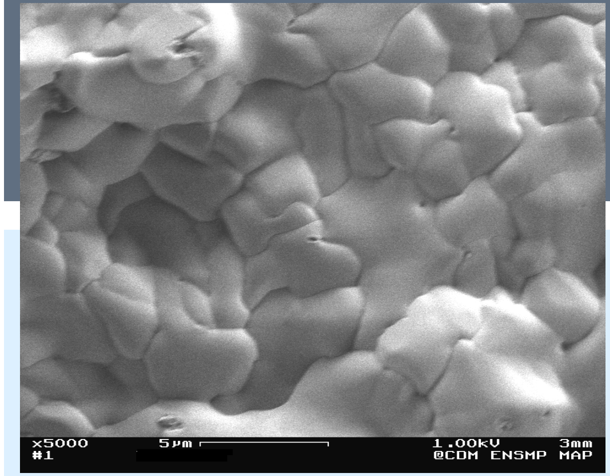


In distilled water
Star-like morphology
Nano sub-units

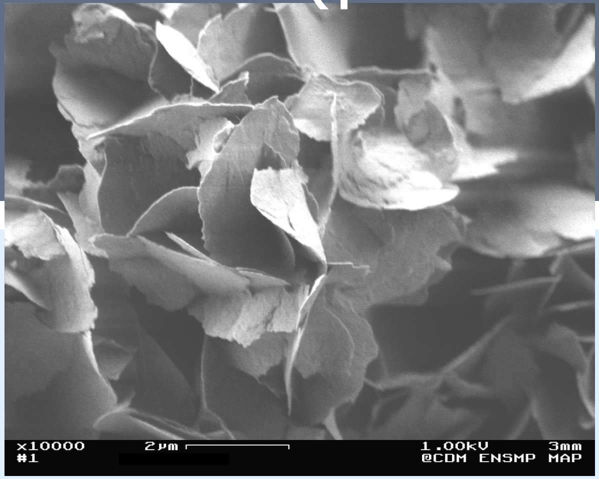
Sodium sulphate solution
menhirs
100nmx200nm
200nmx450nm

SDS solution :
Sticking by the basis
50nmx100nm
100nmx350nm

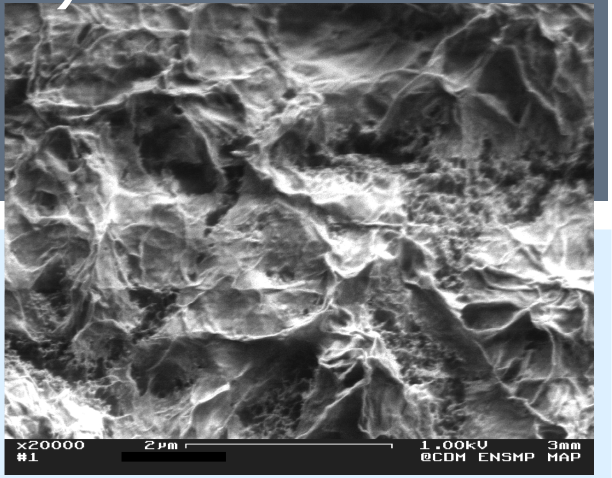
Kinetics (pH=10.5)



5min

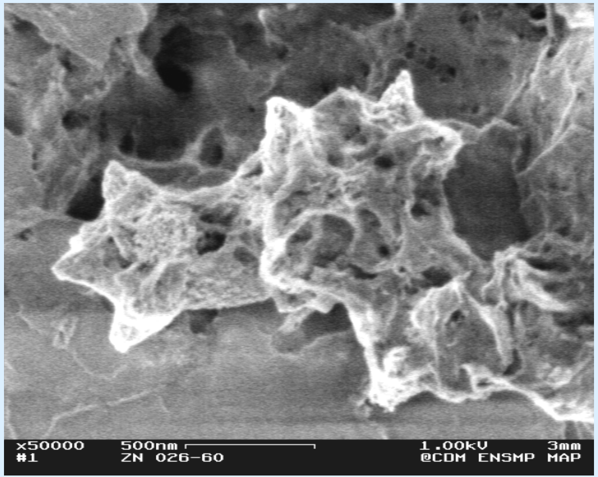


15min

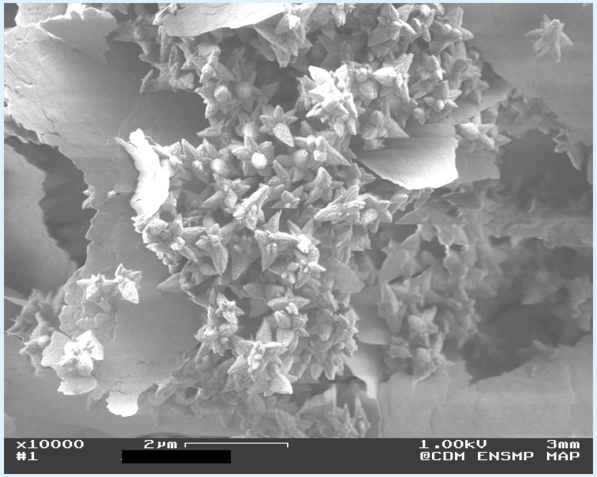


30min

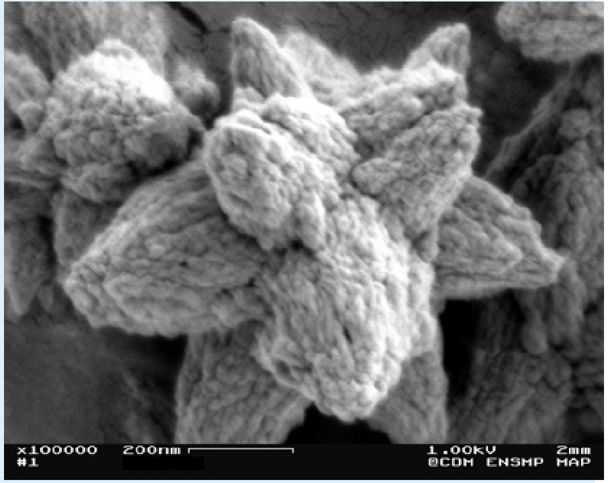
Time (min)



60min



90min

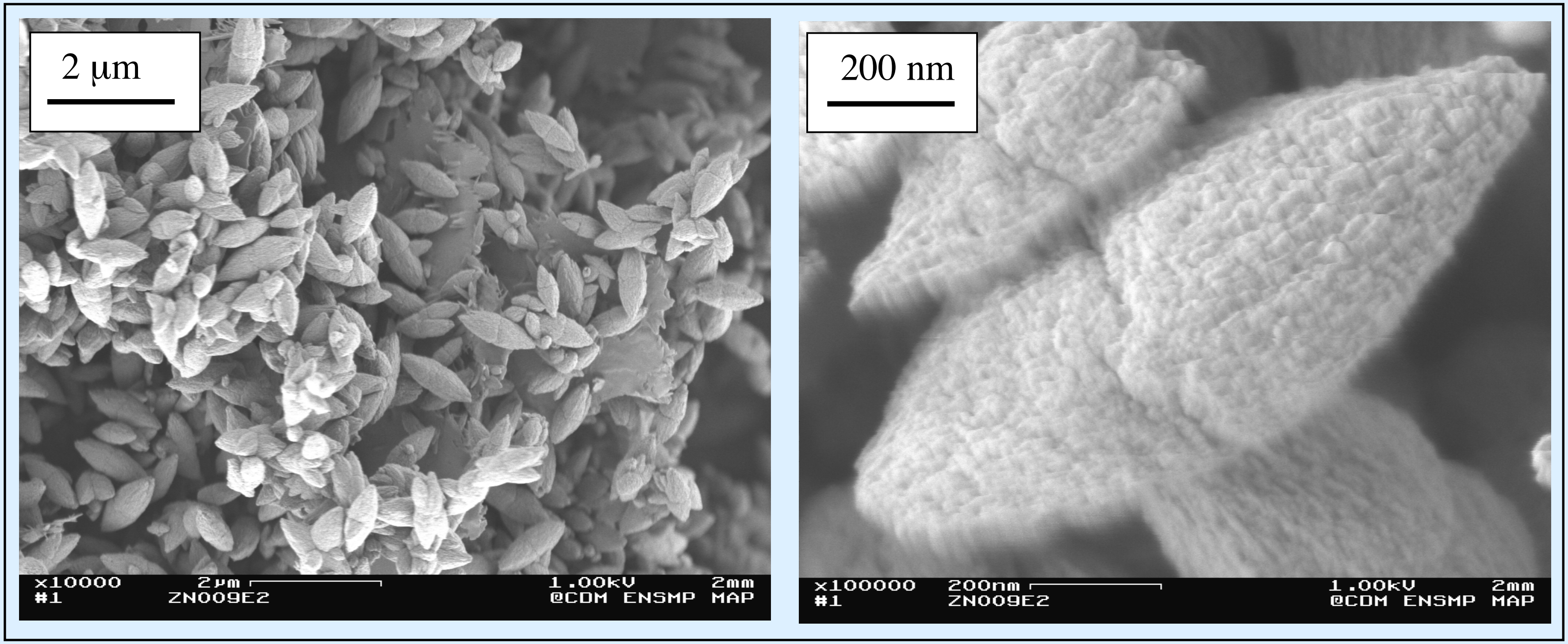


120min

Temps (min)

ZnO: pH influence (double jet)

Same precipitation conditions as before (25°C), slight pH change: : pH= 9.5



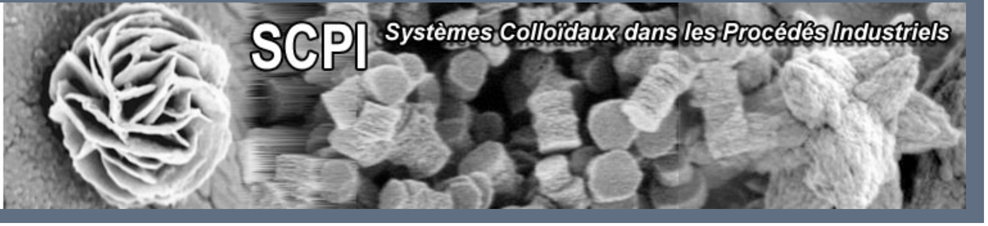
-Cones assembled by the basis
-Oriented nanoparticles build the cones

cristallization of amorphous precipitate

COLLOIDAL SUSPENSIONS OF PEROVSKITE SOLID-SOLUTION NANOPARTICLES FOR ENERGY CONVERSION TECHNOLOGIES

R. P. Doherty[1], I. Dozov[2], P. Davidson[2], M-H. Berger[3], T. Delahaye[1],
J-F. Hochepied[1]

[1] Systèmes Colloïdaux dans les Procédés Industriels, CEP, Mines ParisTech, ENSTA ParisTech, France
[2] Laboratoire de Physique des Solides, Université Paris-Sud, France
[3] Centre des Matériaux, Mines ParisTech, France



Why $KNbO_3$-$BaTiO_3$?

Proven ferroelectrics

$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$
aka PMN-PT

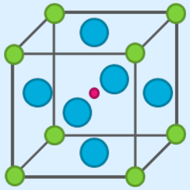
$Pb[Zr_xTi_{1-x}]O_3$
aka PZT

→ **Lead free** →

T_{Curie} $BaTiO_3$ = 130 °C
$KNbO_3$ = 430 °C

↓

Solid Solution



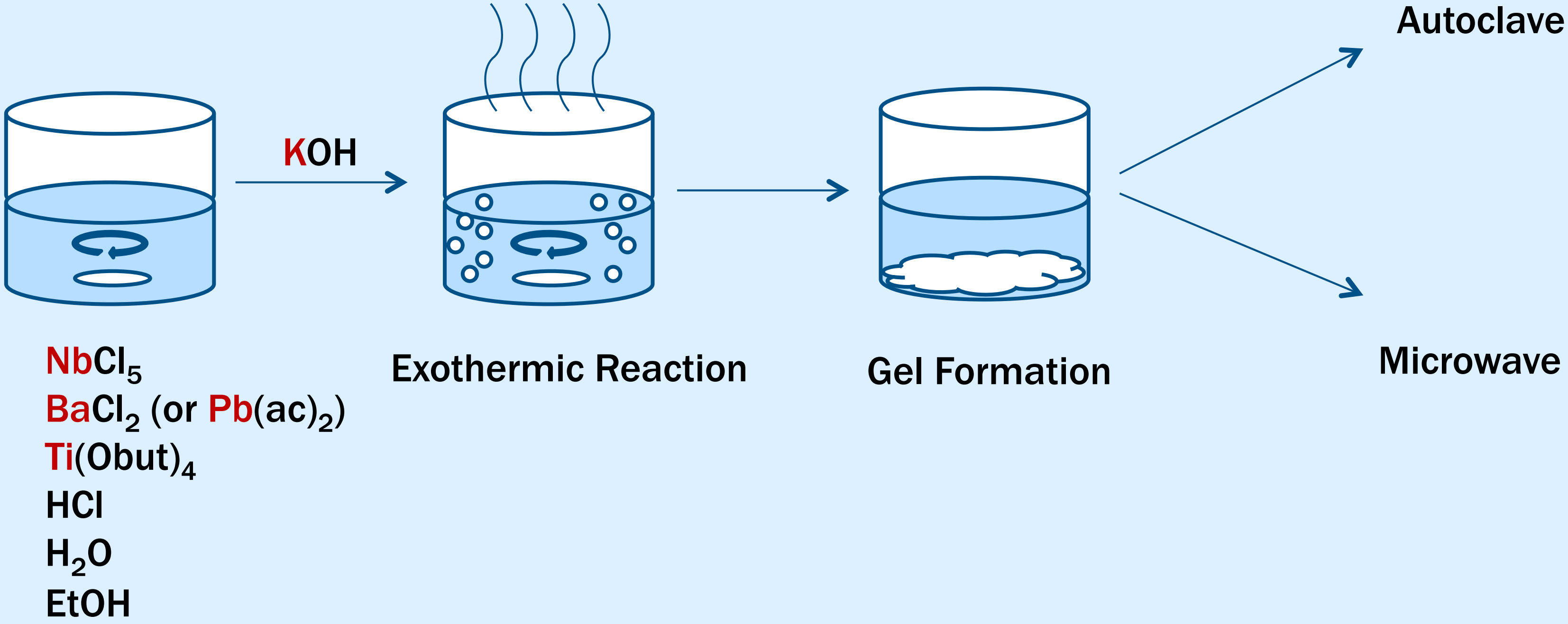
● Ba^{2+} ● Ti^{4+} ● O^{2-}

or

● K^{+} ● Nb^{5+} ● O^{2-}

T_{Curie} → Ferroelectric becomes paraelectric → No spontaneous polarisation

Nanoparticle synthesis



$NbCl_5$
$BaCl_2$ (or $Pb(ac)_2$)
$Ti(Obut)_4$
HCl
H_2O
EtOH

KOH

Exothermic Reaction

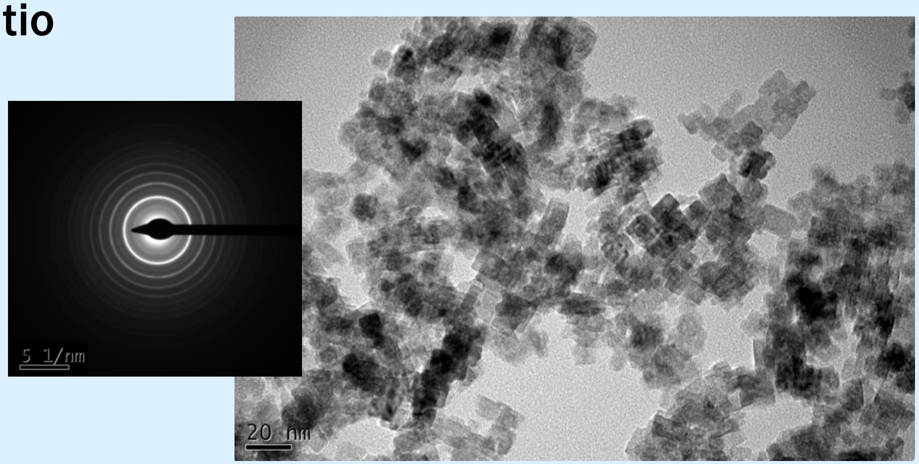
Gel Formation

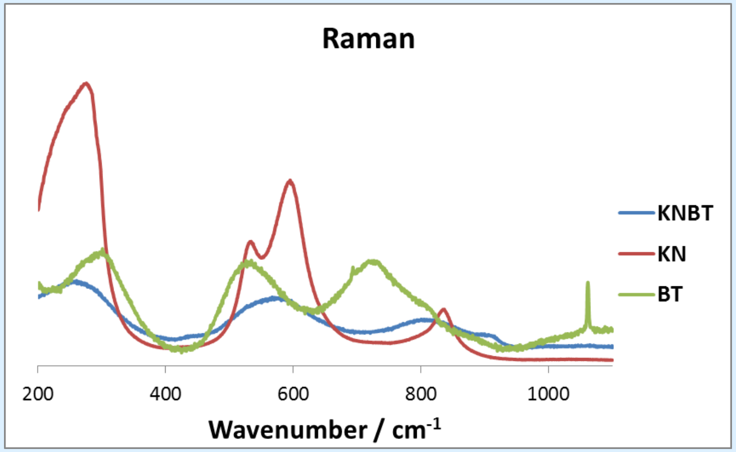
Autoclave

Microwave

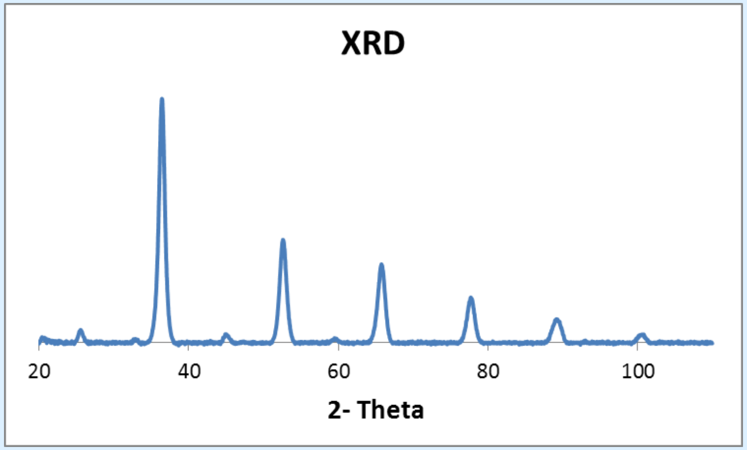
KNBT CHARACTERISATION

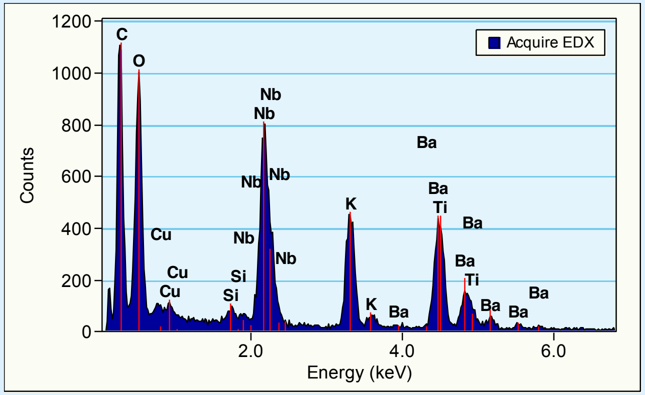
ratio





BET Surface : 100 m^2g^{-1}





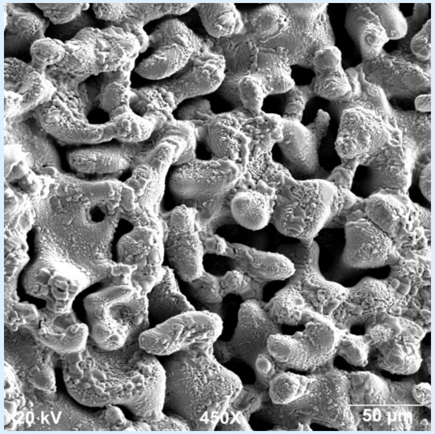
ENGINEERING OF THERMOELECTRIC PROPERTIES IN THE TIO_2 - SNO_2 SYSTEM

F. Dynys[1], M.H. Berger[2], J.F Hochepied[2], A. Sayir[1,3] and A. Sehirlioglu[3]

[1]NASA Glenn Research Center
[2]Mines ParisTech
[3]Case Western Reserve University

NASA-IVHM
AFOSR (EOARD Grant # 073031)
NASA-Hypersonics (NNX08AB34A)

Toward dense Sn rich composition



- Starting from TiO_2 and SnO_2 powders →
- Low densification of SnO_2 based compounds

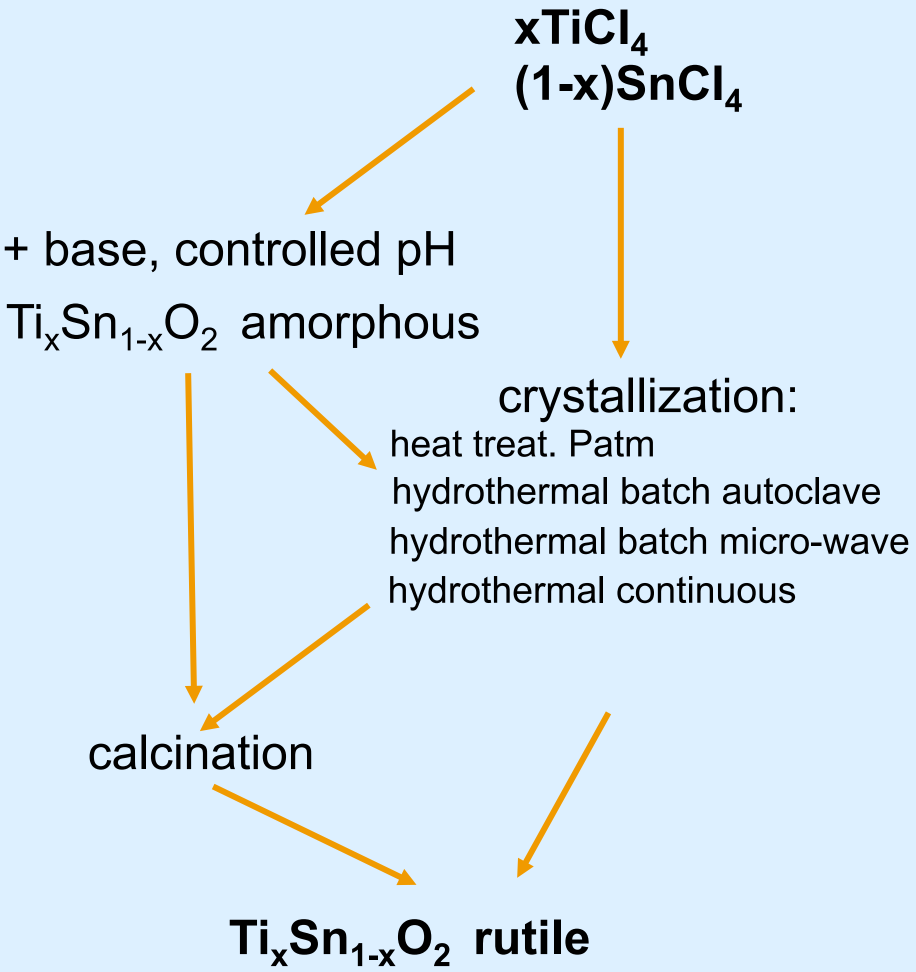
Surface diffusion – Evaporation

- favorable for gas sensors …
- detrimental for electronic conductivity

→ starting from powders with an atomic scale mixing of Ti and Sn

Which Densification ???

$Ti_xSn_{1-x}O_2$ nanopowders by a Co-Precipitation route



$xTiCl_4$
$(1-x)SnCl_4$

+ base, controlled pH

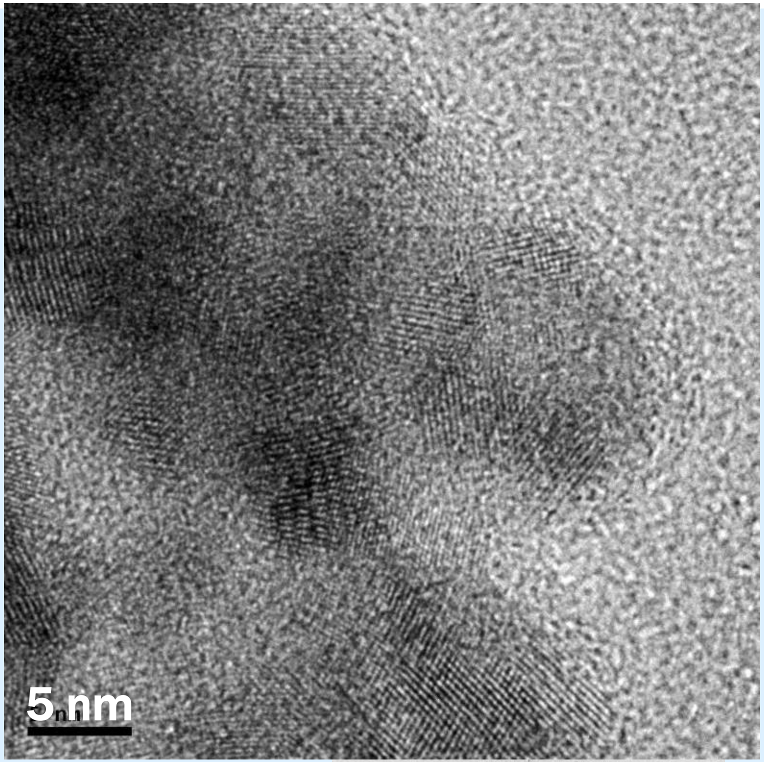
$Ti_xSn_{1-x}O_2$ amorphous

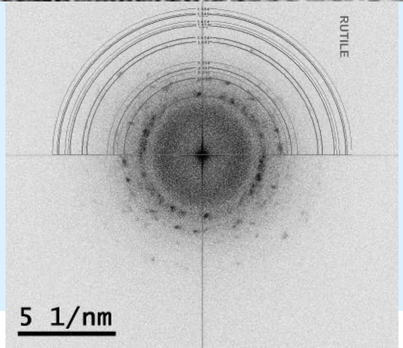
crystallization:

heat treat. Patm
hydrothermal batch autoclave
hydrothermal batch micro-wave
hydrothermal continuous

calcination

$Ti_xSn_{1-x}O_2$ rutile



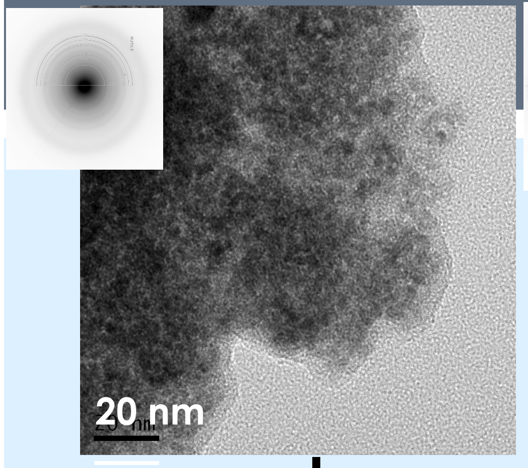


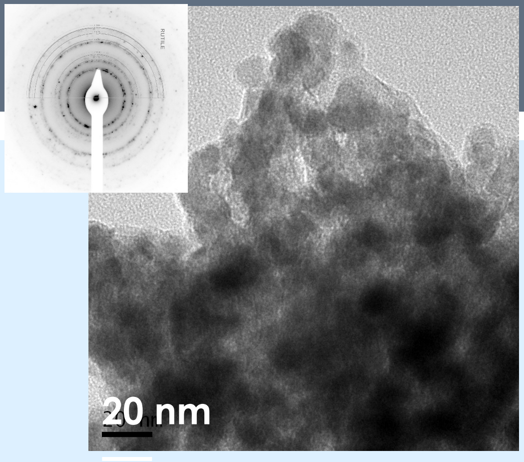
Calcined 500°C

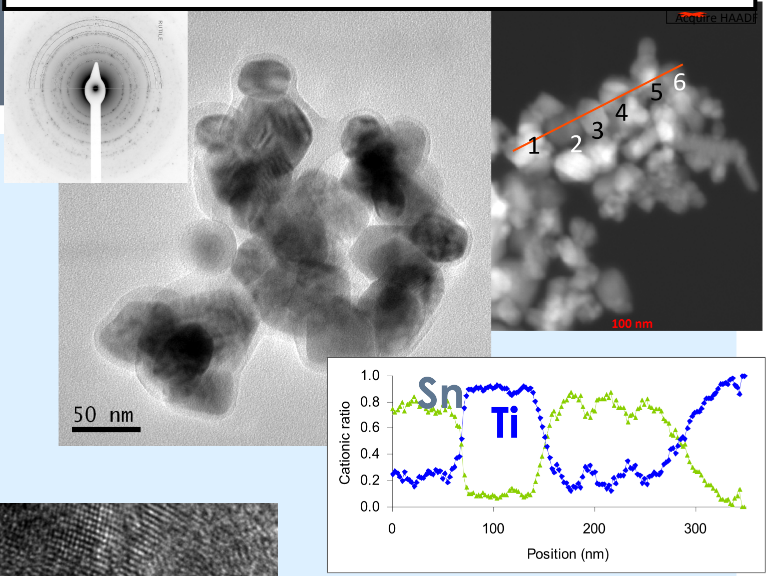
precipitate
→ 2nm rutile, solid solution

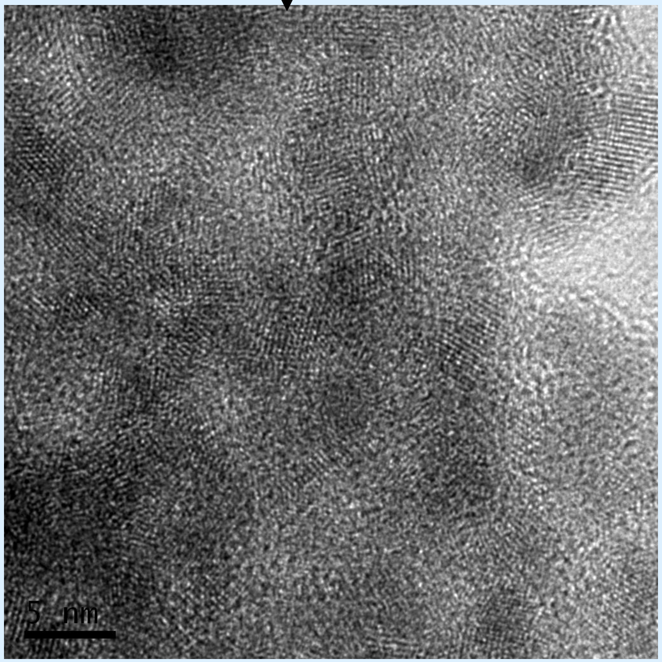
600°C 3H → 20nm rutile solid solution

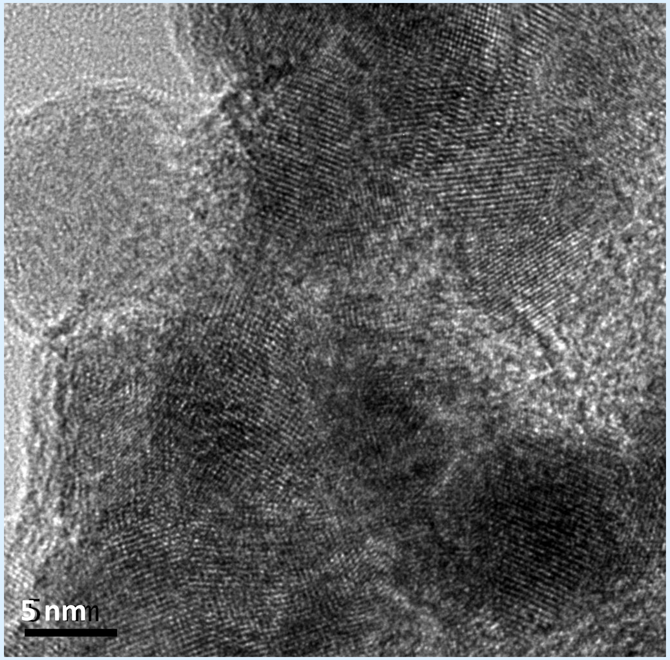
850°C 3H
→ 50nm Ti enriched + Sn enriched





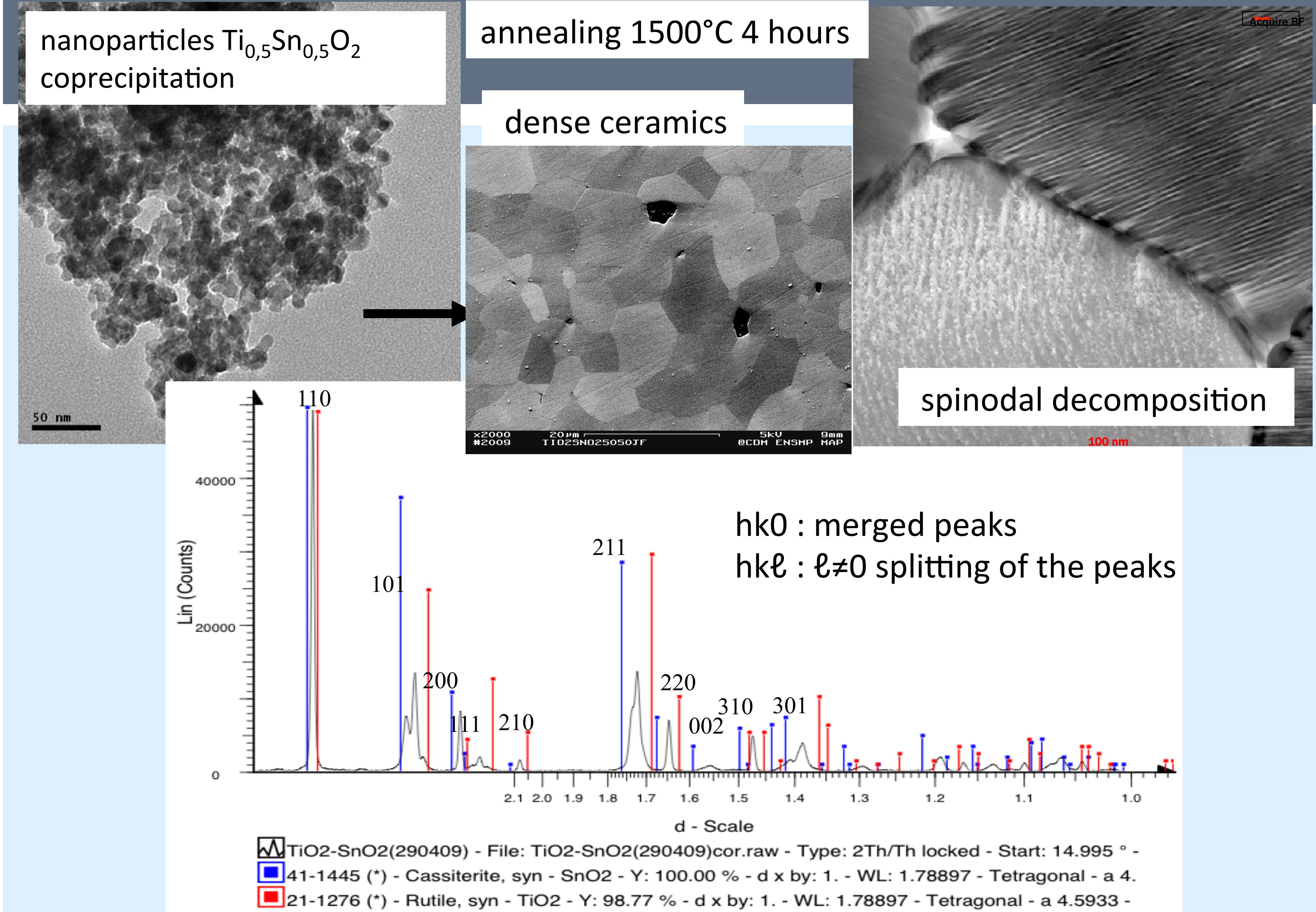






precipitation rutile nano + calcination: Rutile growth-demixion Ti-Sn

CERAMICS



nanoparticles $Ti_{0,5}Sn_{0,5}O_2$
coprecipitation

annealing 1500°C 4 hours

dense ceramics

spinodal decomposition

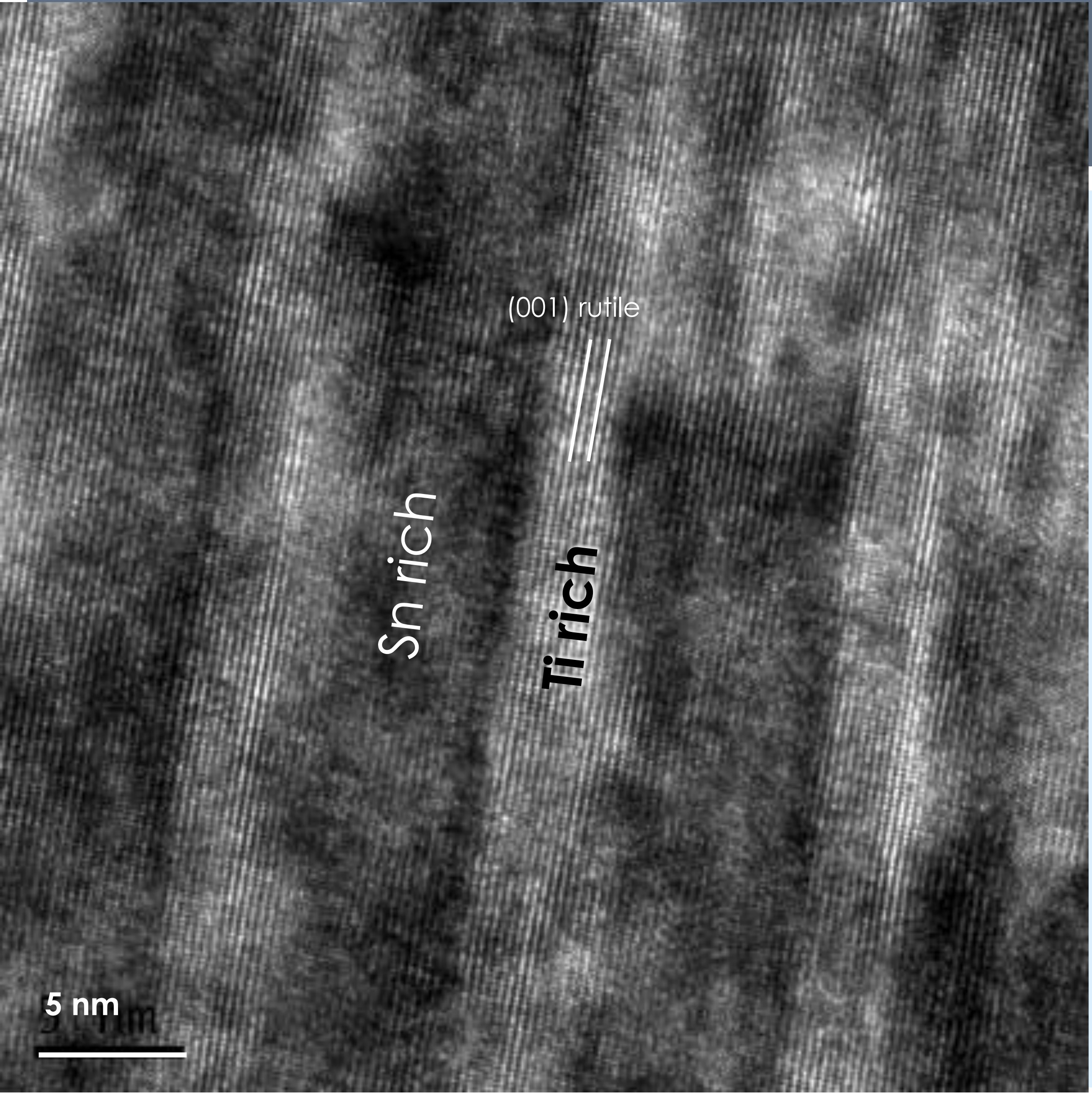
hk0 : merged peaks

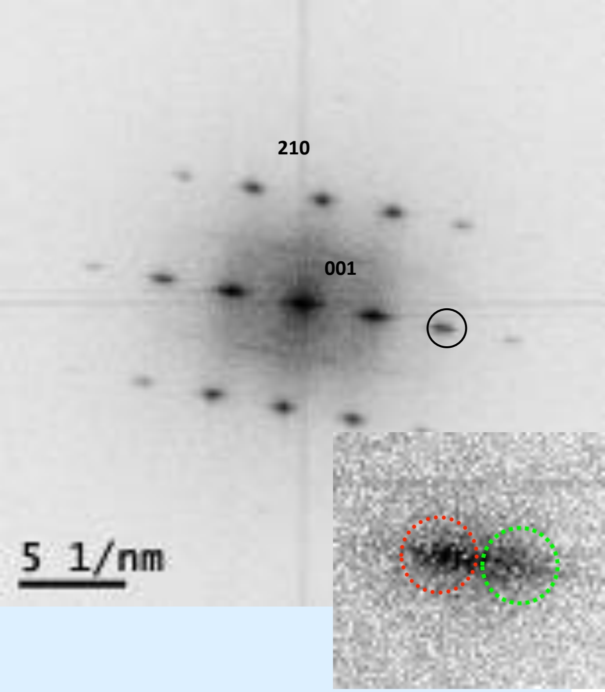
hkℓ : ℓ≠0 splitting of the peaks

Coherent Interfaces // (001)

a & b $_{\text{Sn rich}}$=a & b $_{\text{Ti rich}}$

$c_{\text{Sn rich}} > c_{\text{Ti rich}}$





CONCLUSIONS

Aqueous chemistry vs. Non aqueous chemistry:

Non aqueous chemistry: triumphes over aqueous chemistry for some materials as perovskites, smaller sizes, monodispersity and better crystallinity

Aqueous chemistry: close to industrial concern (costs, scale-up). Many opportunities