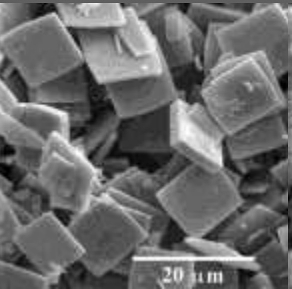
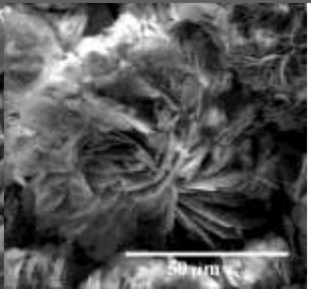
UMR - CNRS 7574
Laboratoire Chimie de la Matière Condensée de Paris,
Site Collège de France
Groupe Nanomatériaux Inorganiques

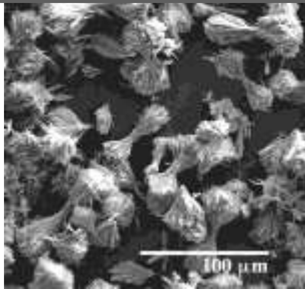
Metal oxide nanoparticles: Synthesis and Reactivity

Corinne Chanéac

Environmental Nanotechnologies, 7-8 July 2011, Aix en Provence, France







Stage 1: List of Endpoints

- Nanomaterial Information/Identification
- **Physical-Chemical Properties and Material Characterization**
- Environmental Fate
- Environmental Toxicology
- Mammalian Toxicology
- Material Safety

ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT
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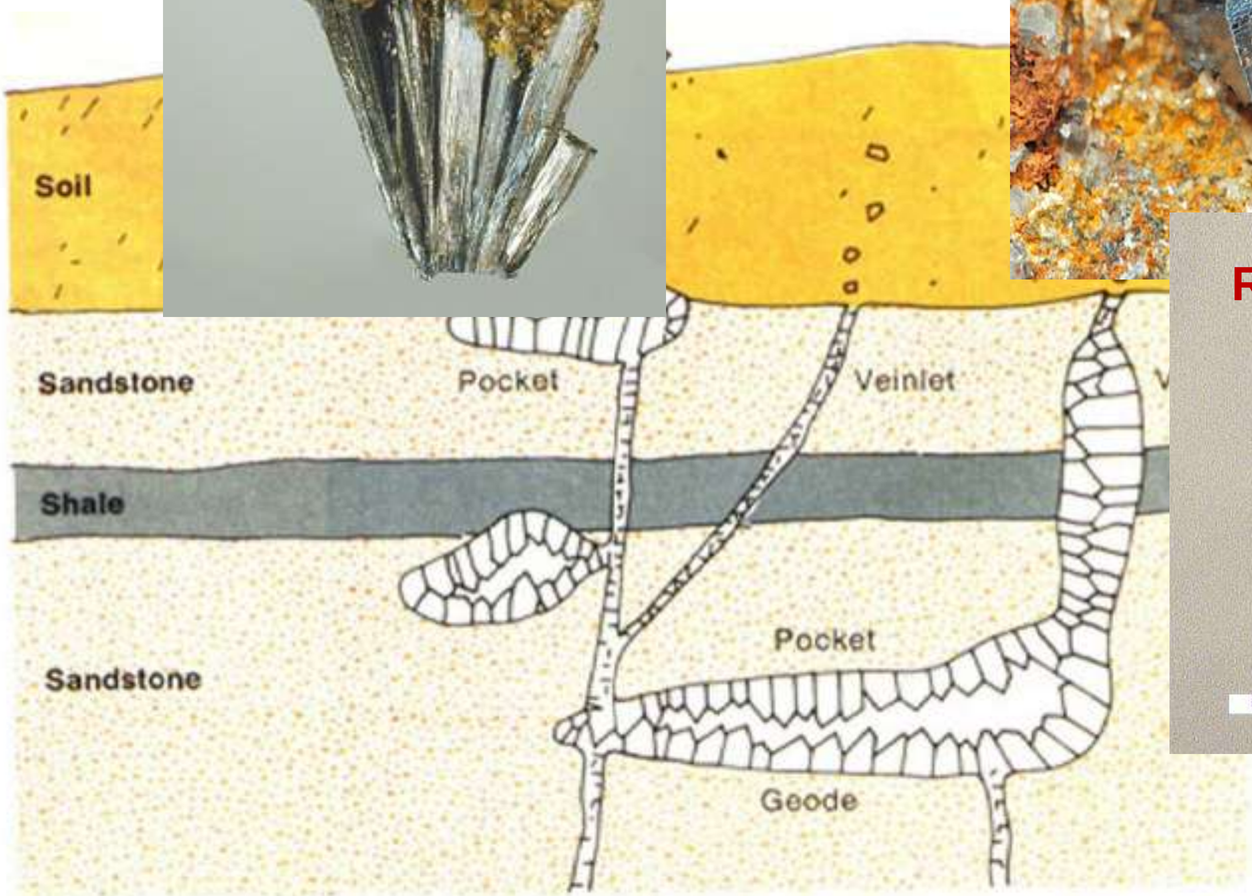
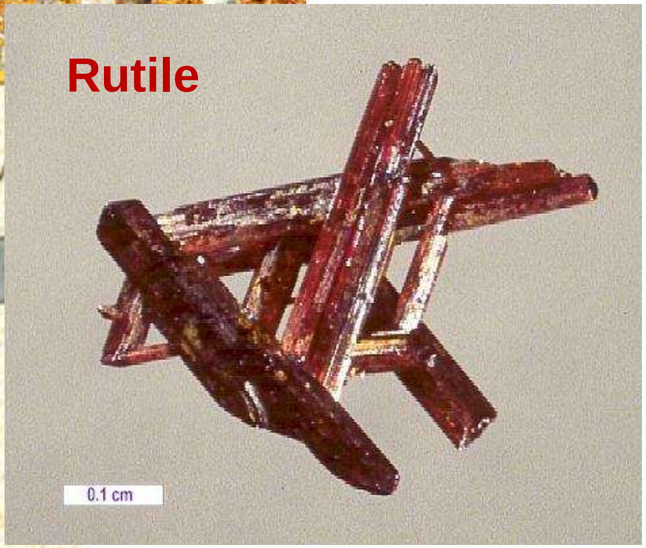
List of Manufactured Nanomaterials (14)

- Fullerenes (C60)
- Single-walled carbon nanotubes (SWCNTs)
- Multi-walled carbon nanotubes (MWCNTs)
- Silver nanoparticles
- Iron nanoparticles
- Carbon black
- **Titanium dioxide**
- **Aluminium oxide**
- Cerium oxide
- Zinc oxide
- Silicon dioxide
- Polystyrene
- Dendrimers
- Nanoclays

Soft Chemistry

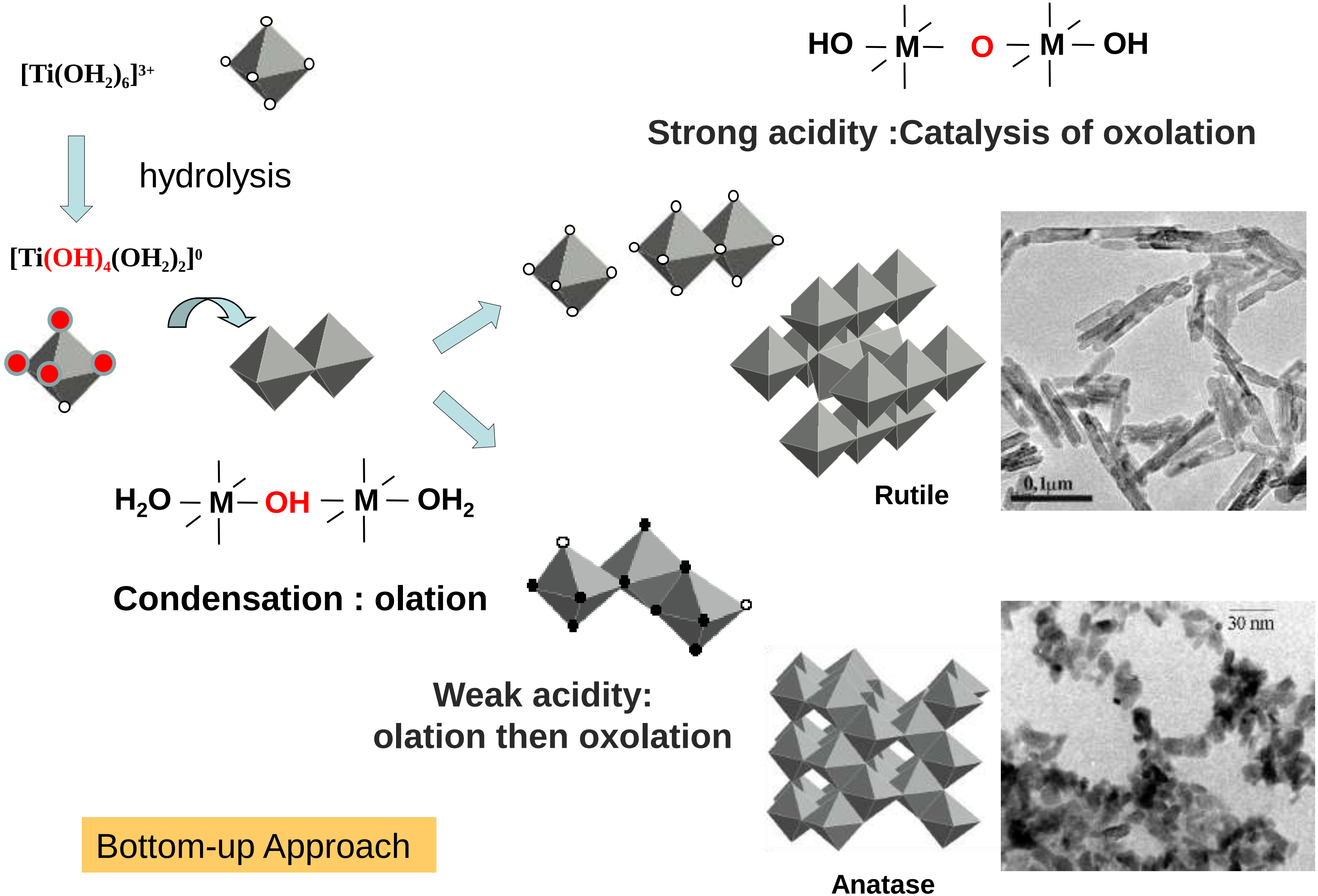
Morphology and Nanoparticles



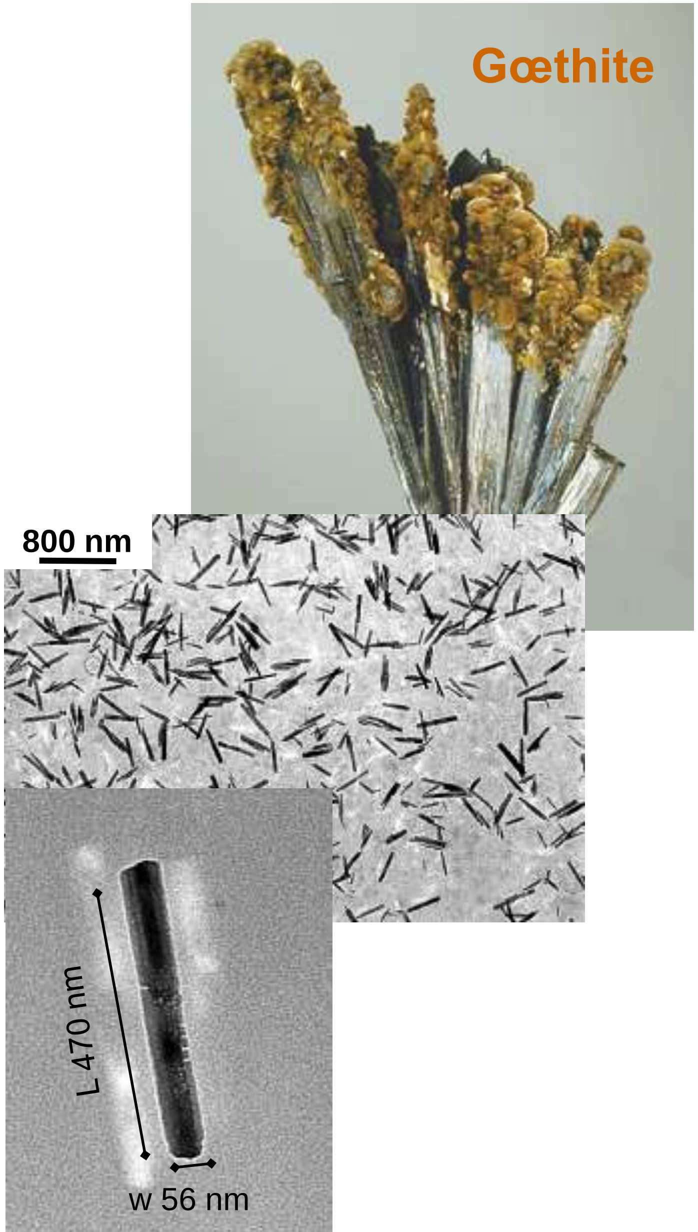


Formation of natural crystals in geological conditions

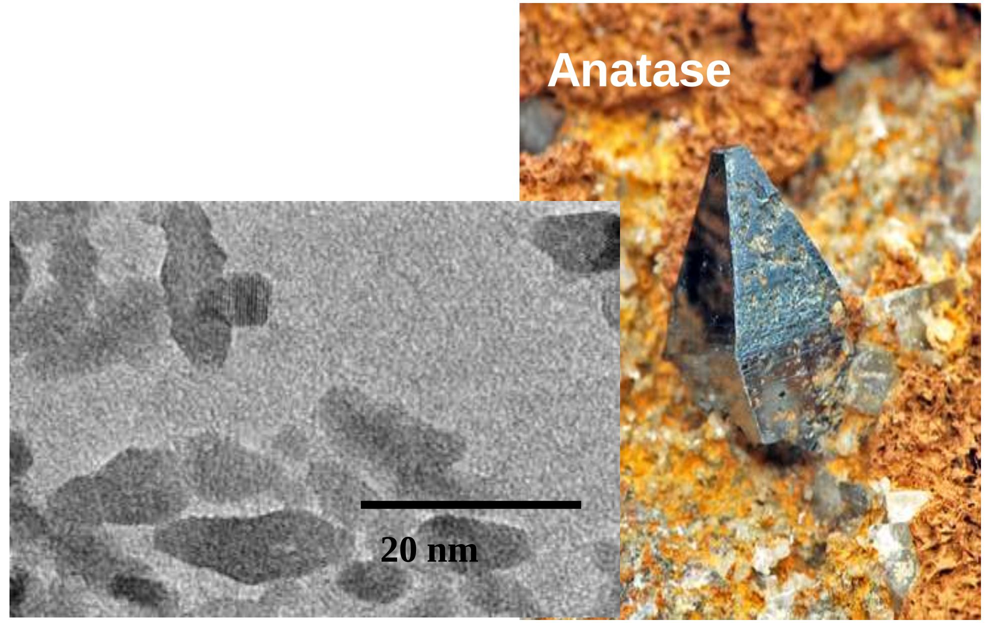
Aqeous Sol-Gel Process for nanoparticle synthesis



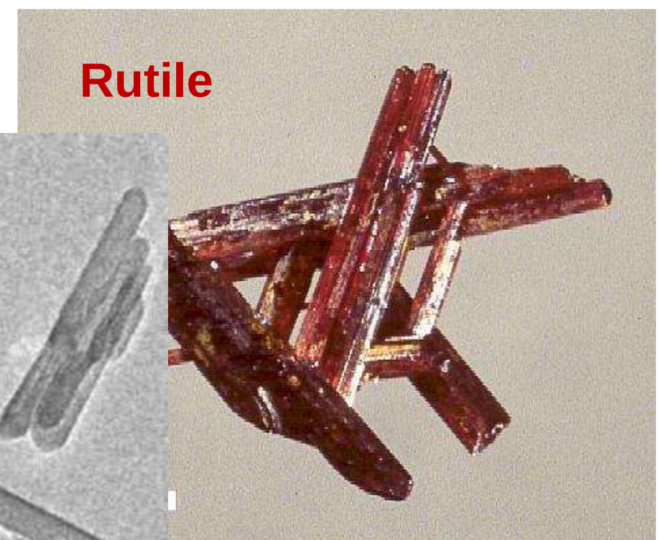
Morphology and Nanoparticles

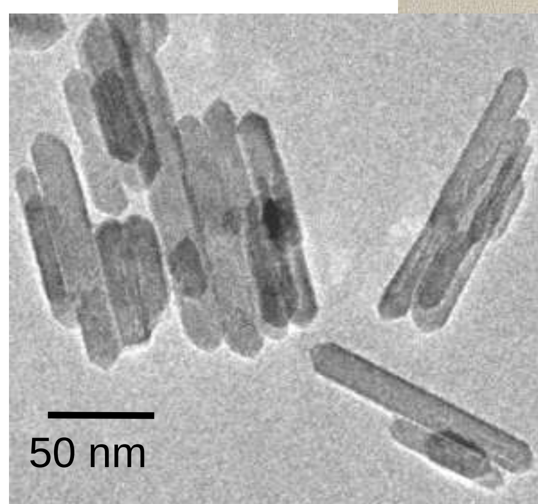


Chem. Comm., 5, **2004**, pp. 481-487



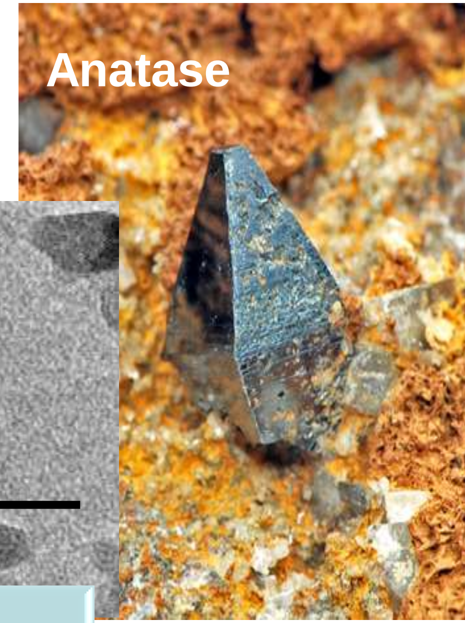
Durupthy, O.; Bill, J.; Aldinger, F. Cryst. Growth Des. ***2007****, 7, 2696*

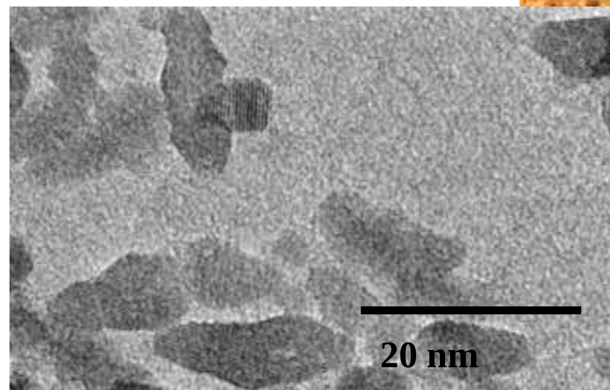




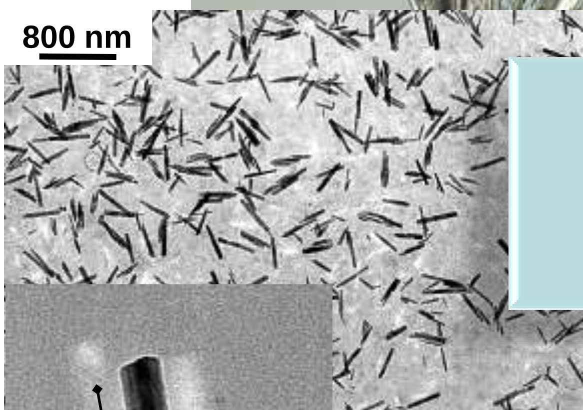
JACS*, 2007,129 (18),5904*

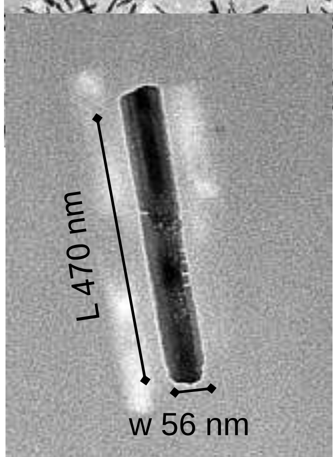
Morphologie et Nanoparticules



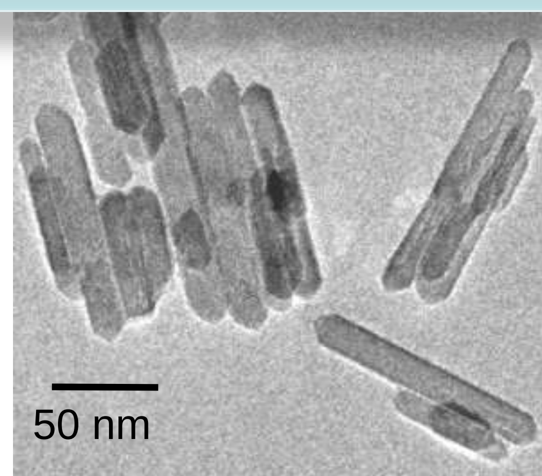


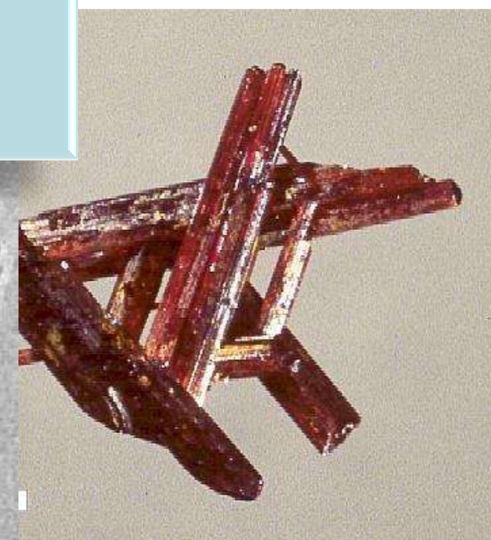
rowth Des. ***2007***, *7, 2696*





How control the nanocrystal growth?

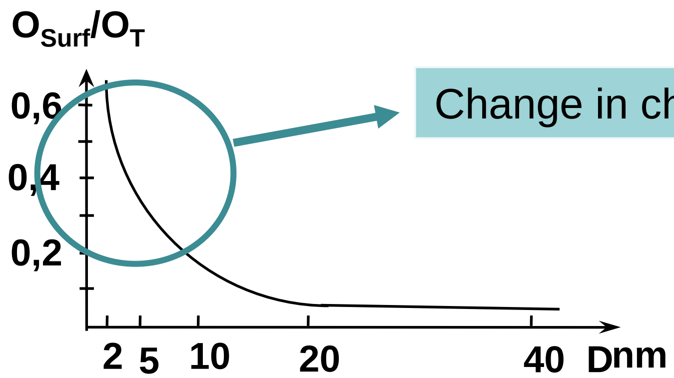




Chem. Comm., 5, **2004**, pp. 481-487

JACS, *2007,129 (18),5904*

Surface energy : origin



Change in chemical and physical properties

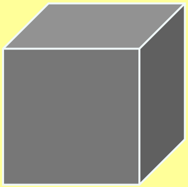
Solid formation

$$\Delta G_{formation}^{\circ} = n\Delta G^{\circ}_{Bulk} + \Delta G^{\circ}_{surface}$$

$\Delta G^{\circ}_{surface} > 0$

Variation of surface energy with the particle size (Sodium Chloride):

Side (cm)	Total Surface aera (cm²)	Surface Energy (J/g)
0,1	28	$5{,}6.\ 10^{-4}$
0,01	280	$5{,}6.\ 10^{-3}$
10^{-4} (1µm)	$2{,}8.\ 10^{4}$	0,56
10^{-7} (1nm)	$2{,}8.\ 10^{7}$	560



Calculation for a cube of Sodium Chloride

Surface Sci. 60, 445, 1976

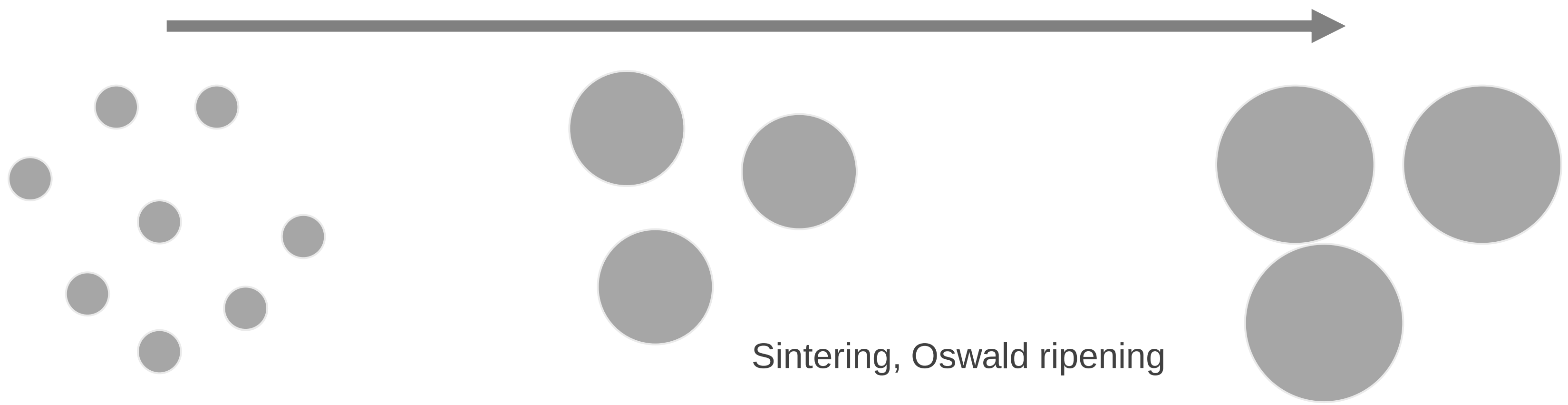
Huge surface energy for nano-solids - Thermodynamically unstable system

Surface energy : origin

Unstability of nanometric colloidal dispersion:

$\Delta G° = n\Delta G°_{Bulk} + \Delta G°_{surface}$

E surface ↘ : stability ↗



Spontaneous evolution of nanoparticles to minimise the surface contribution

Surface : motive power of growth

How determine the surface energy?

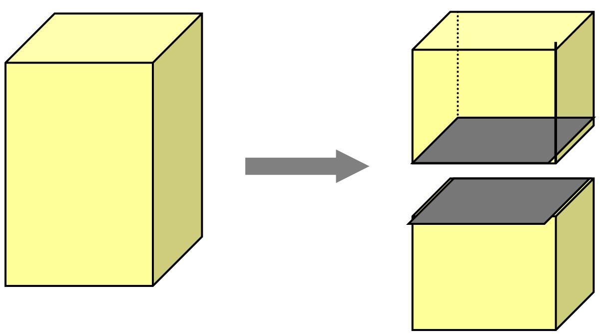
Surface energy : origin

$$\Delta G° = n\Delta G°_{Bulk} + \Delta G°_{surface}$$

$$\gamma = (\delta G/ \delta A)_{n_i, T, P}$$

γ : surface energy

energy requiered to create an unit of aera



Bond strength

$$\gamma = \tfrac{1}{2} N_b \, \varepsilon \, \rho_a$$

Surface atomic density

Number of broken bonds per atom

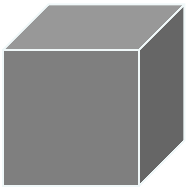
Rough estimation of surface energy:

- surface relaxation
- surface restructuring with formation of new chemical bond
- same value of ε for all the atoms
- no entropic consideration/ pressure or volume

Surface Sci. 60, 445, 1976

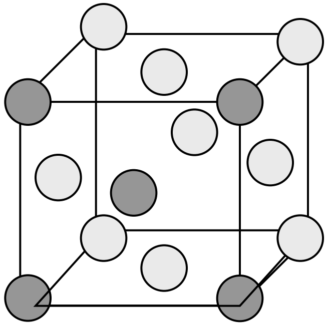
Origine de l'énergie de surface

$$\gamma = \frac{1}{2} N_b \, \varepsilon \, \rho_a$$

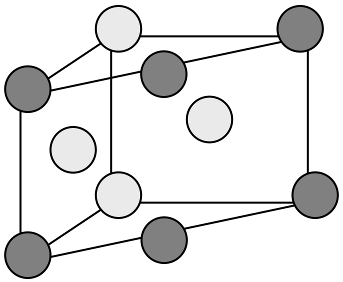


FCC Structure
Coordination number of 12
Lattice parameter a

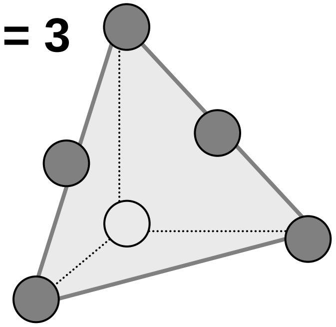
$N_b = 4$



$N_b = 5$



$N_b = 3$



$$\gamma_{\{100\}} = \frac{1}{2}\, 2/a^2 . 4 . \varepsilon = 4\, \varepsilon / a^2$$

$$\gamma_{\{110\}} = 5\varepsilon / \sqrt{2}\, a^2 = 3{,}52\, \varepsilon / a^2$$

$$\gamma_{\{111\}} = 2\sqrt{3}\varepsilon / a^2 = 3{,}46\, \varepsilon / a^2$$

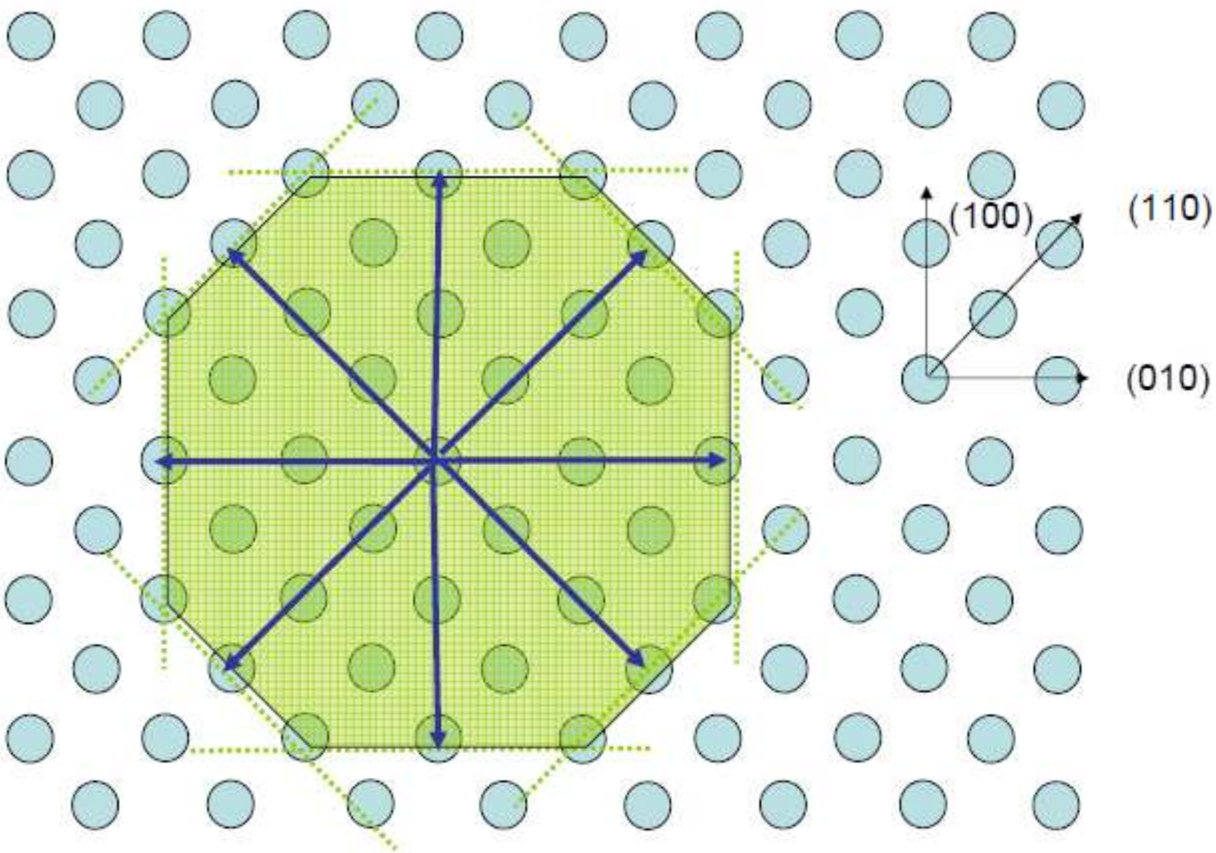
Surface energy depends of the index of facets :

⟹ **low index facets = low surface energy**

Relation between surface energy and crystal shape

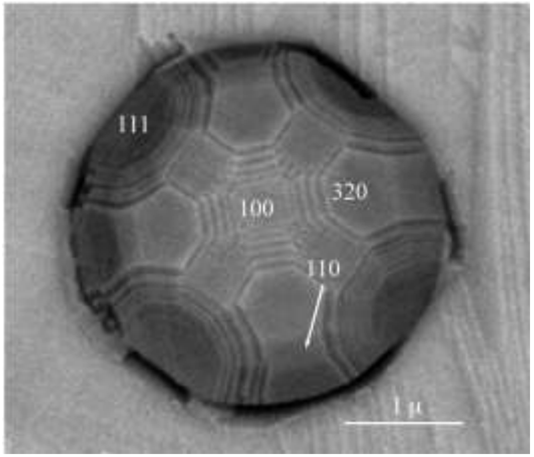
Shape of nanoparticle : total surface energy reaches minimum

→ Wulff construction



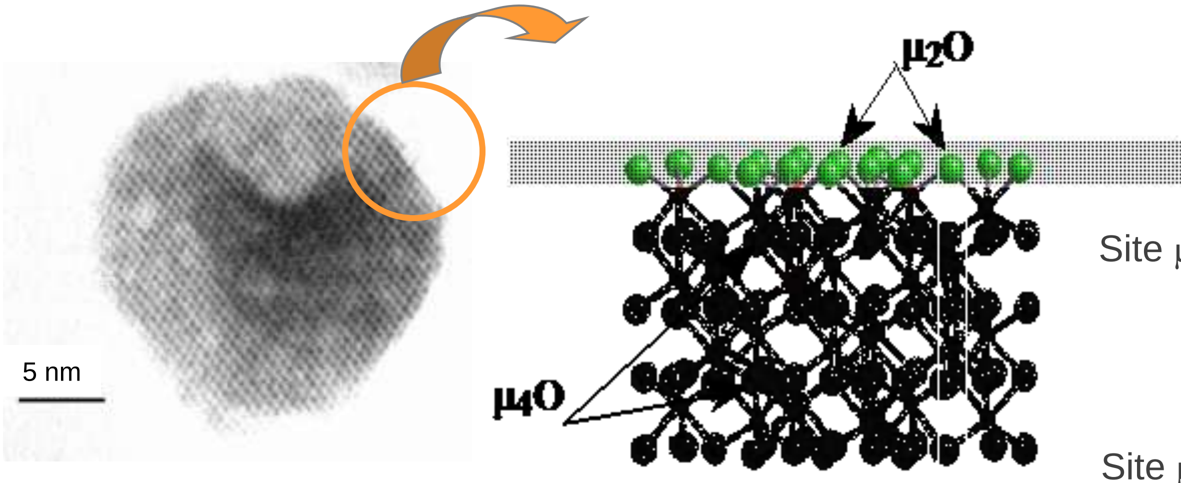
Morphologies for a 2D crystal for 10 and 11 faces

Equilibrium crystal

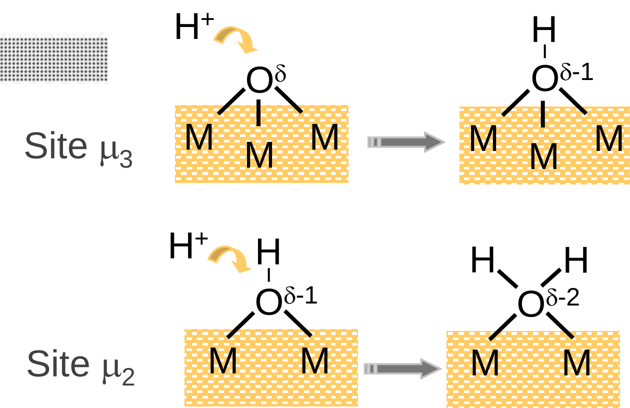


Bi doped with Cu

Surface energy at the atomic scale



Brønsted basic site



T. Hiemstra et al., J. Colloid Interface Sci. 184, 680 (1996)

Model of multisite complexation , MUSIC²

$K_{protonation}$ = f (structure, hydratation)

$$M_nO^{(nv-2)} + H^+_{solv} \rightleftharpoons M_nOH^{(nv-1)} \quad K_{n,1}$$

$$M_nOH^{(nv-1)} + H^+_{solv} \rightleftharpoons M_nOH_2^{\ nv} \quad K_{n,2}$$

$$-\mathrm{Ln}\ K_{n,x} = -\ A(\Sigma S_j - 2 + m)$$

$$A = 19{,}8$$

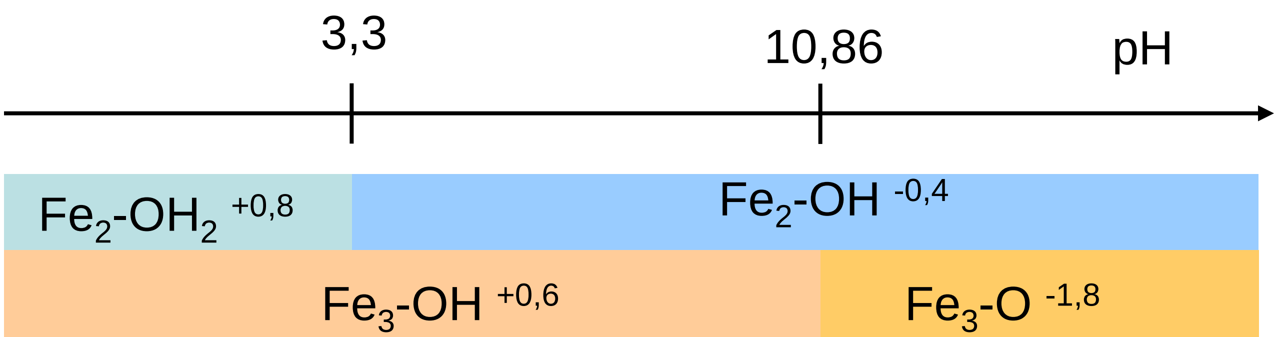
OH μ_1	p+m = 2
OH μ_2	p+m = 1 ou 2
OH μ_3	p+m = 1

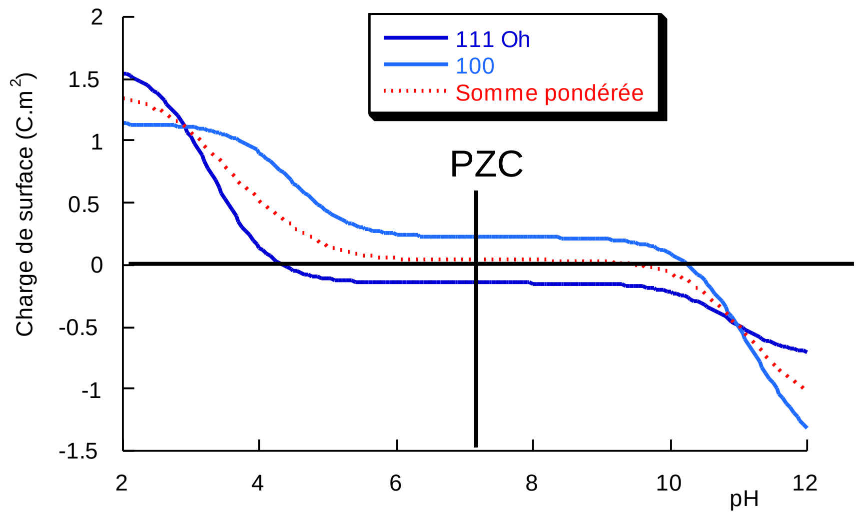
$$\Sigma S_j = \Sigma_i S_{Me} + p\ S_H + m(1 - S_H)$$

$$S_H = 0{,}8$$

Model of multisite complexation , MUSIC²

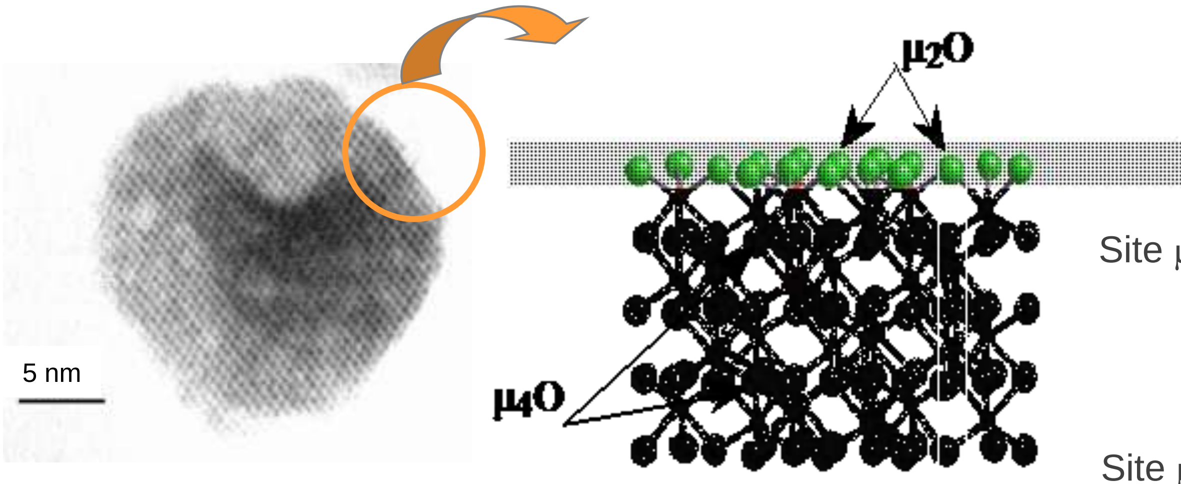
Example : face 111_{Oh} of magnetite, 2 sites μ_2 and μ_3



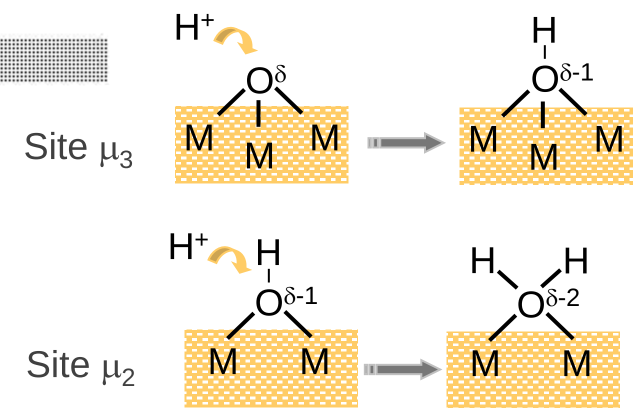


Good valuation of surface charge and of point of zero charge

Surface energy at the atomic scale



Brønsted basic site



T. Hiemstra et al., J. Colloid Interface Sci. 184, 680 (1996)

$\Delta G^\circ_{surface} > 0$ → γA

Gibbs's Law : $\Delta\gamma = -\Sigma_\kappa \Gamma_i d\mu_i$

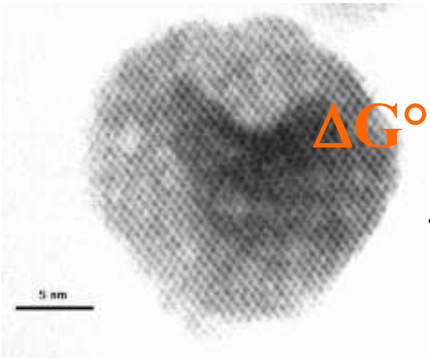
Surface charge density

$$\Delta\gamma = \gamma - \gamma_0 = \frac{RT}{F}\left(0.22\sqrt{I} - 2\sqrt{0.0136\, I + \sigma^2} - \sigma_{max} \right) \ln\left(1 - \frac{\sigma}{\sigma_{max}}\right)$$

J.P. Jolivet et al., J. Mater. Chem., 2004, 14, 3281

Surface Energy Effect

Metastable Object



$$\Delta G^\circ = n\Delta G^\circ_{Bulk} + \Delta G^\circ_{surface}$$

> 0

Two ways

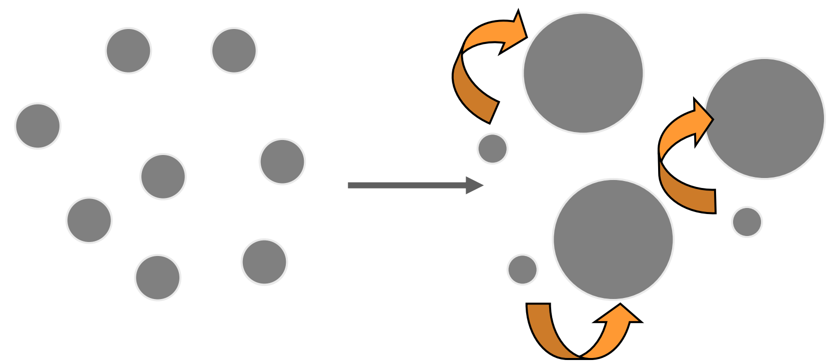
γA

(γ ,surface energy)

(A, surface area)

Decrease of γ

Decrease of A : Oswald ripening



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$$\Delta\gamma = \gamma - \gamma_0 = \frac{RT}{F}\left(0.22\sqrt{I} - 2\sqrt{0.0136 I + \sigma^2} - \sigma_{max}\right) \ln\left(1 - \frac{\sigma}{\sigma_{max}}\right)$$

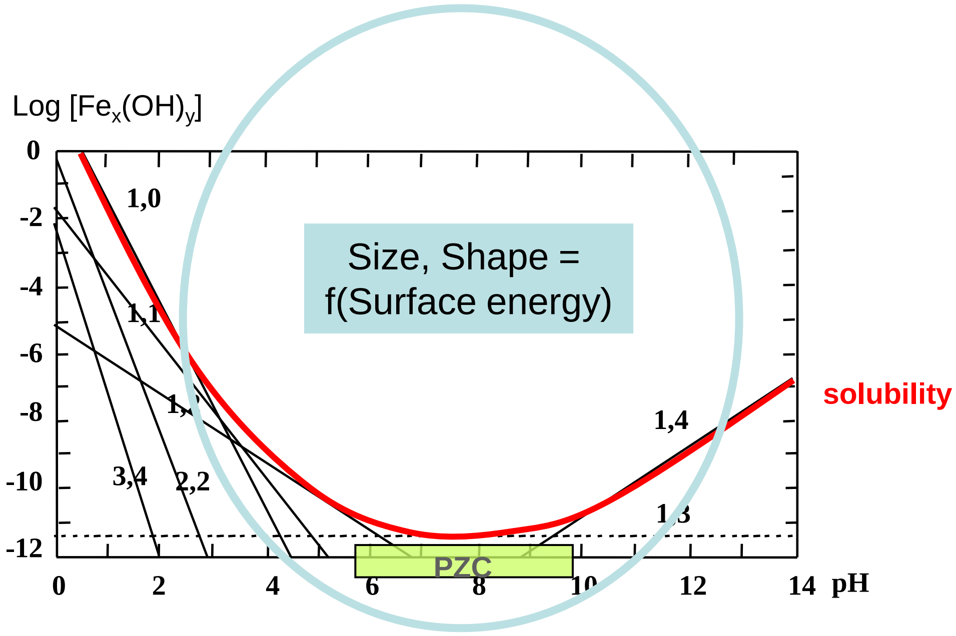
Density of
Surface charge
Previously described

For H>PCN

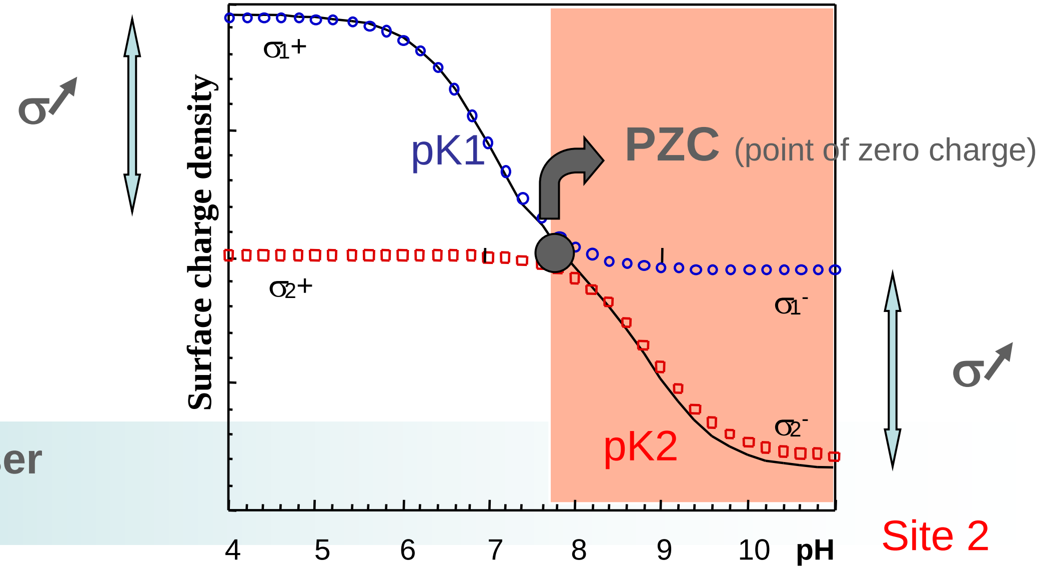
γ decreases when the charge density, σ, increases

J.P. Jolivet et al., J. Mater. Chem., 2004, 14, 3281

Surface Energy Effect



As σ = f(pH)



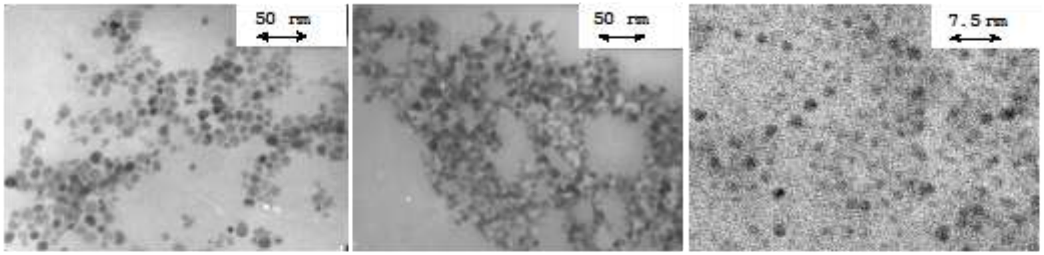
The surface energy is lesser far from the PZC

Isotropic Nanoparticles

Size = f(Surface Energy)

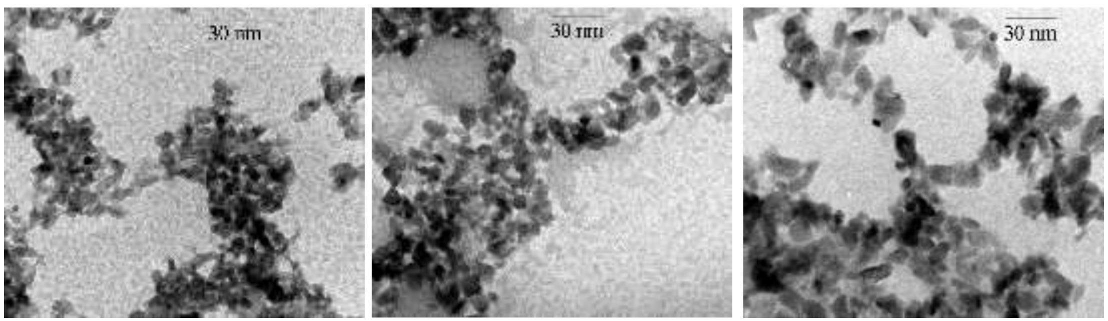
Precipitation of $FeCl_2$ / $FeCl_3$: Fe_3O_4 magnetite

IRM, Hyperthermia



10 **11** **12** **pH**

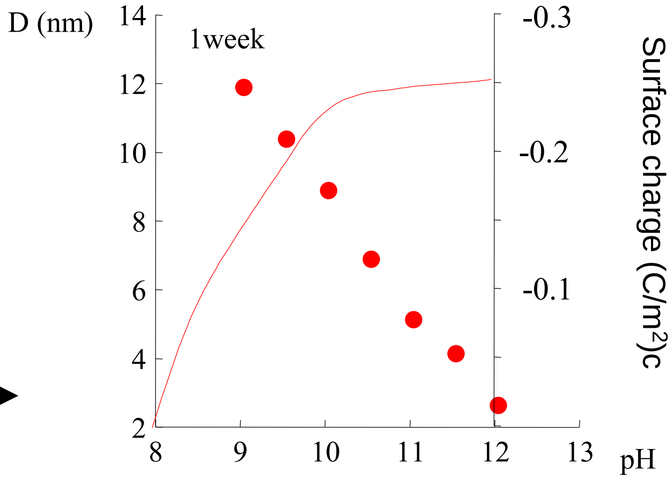
2 **3** **4**

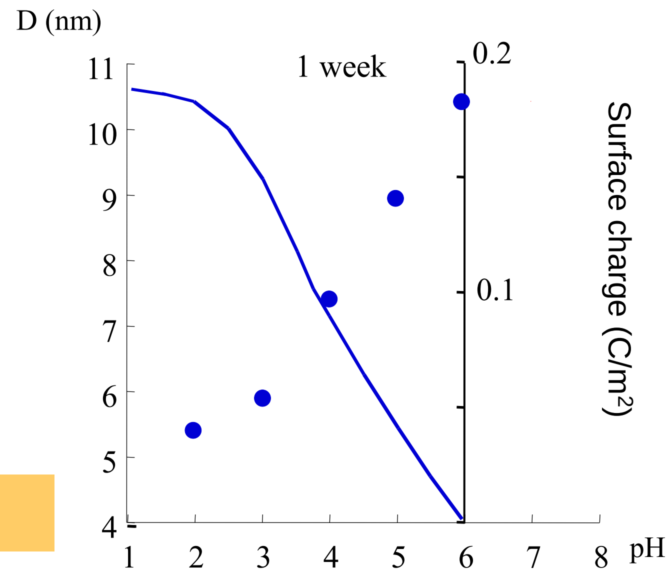


Precipitation of $TiCl_4$: TiO_2 anatase

Photocatalysis, Photovoltaic

Pottier A. (1999), Thèse UPMC, Paris 6





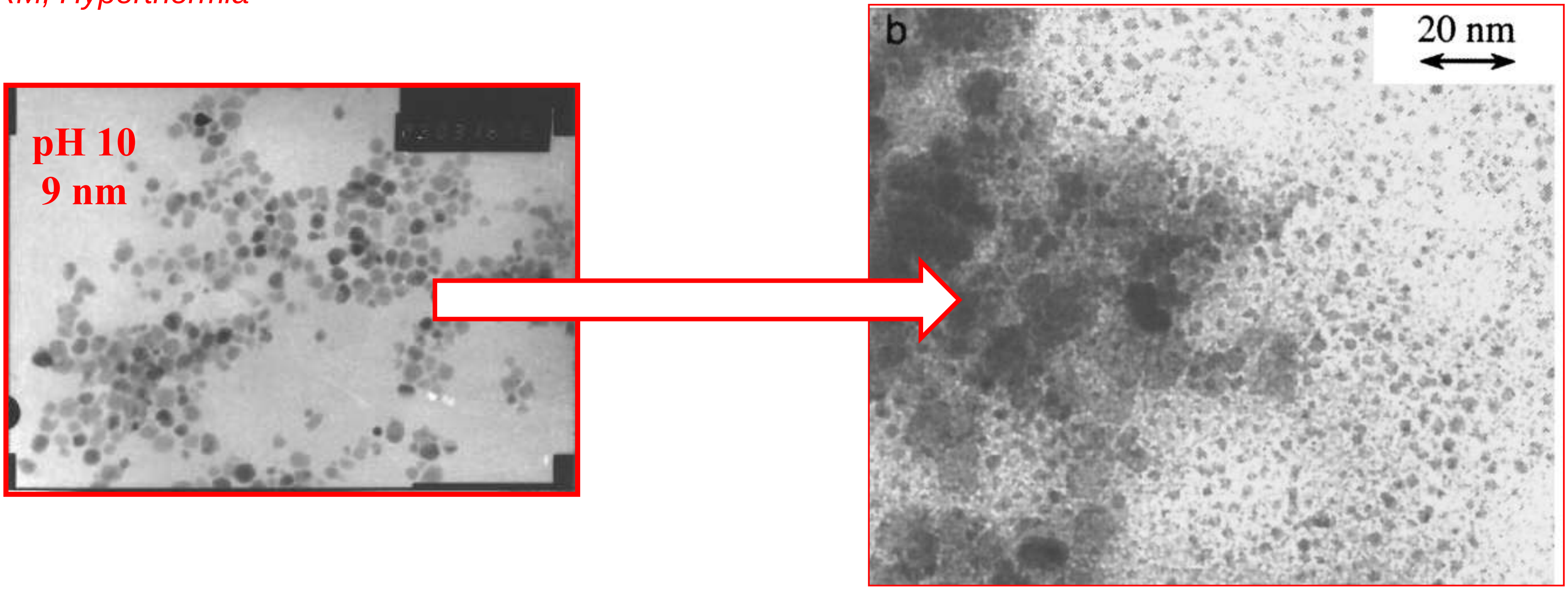
Charged surface = stopped growth

J. of Colloid Interface Sci., 1998, 205, 205 & J. Mater. Chem., 2003, 13, 877

Isotropic Nanoparticles

Size = f(Surface Energy)

Precipitation of $FeCl_2$ / $FeCl_3$: Fe_3O_4 magnetite
IRM, Hyperthermia

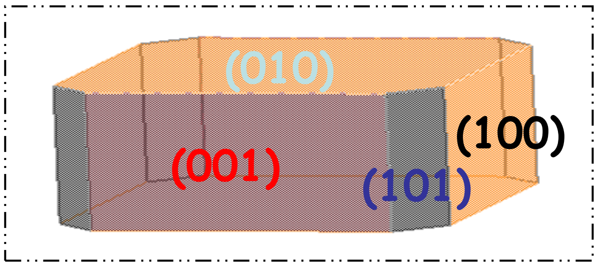


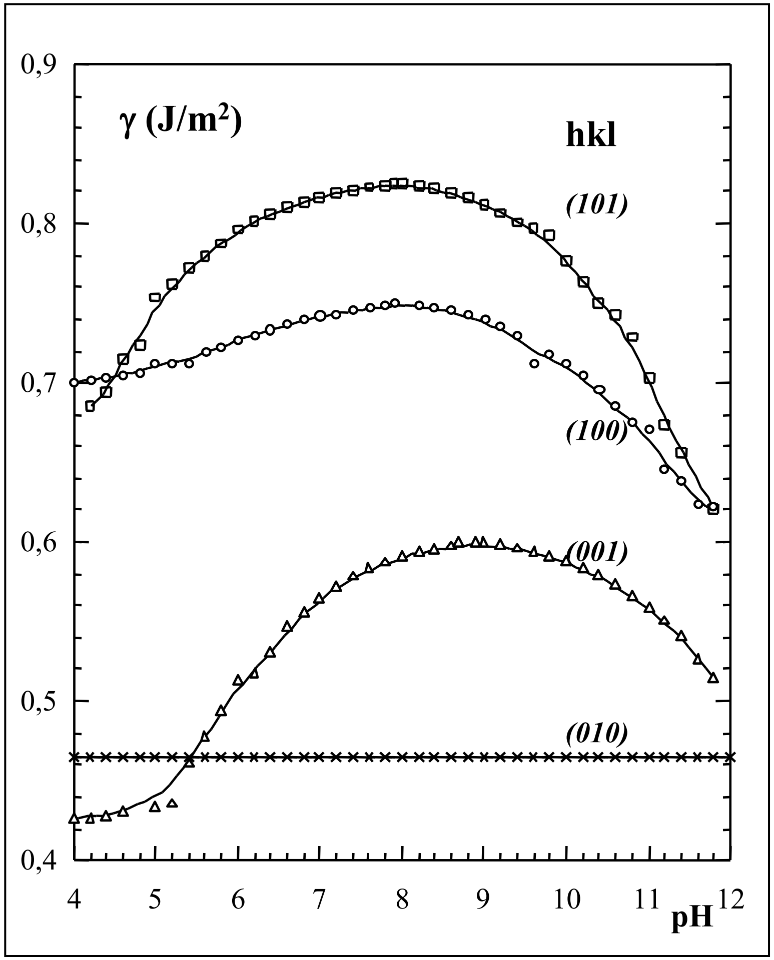
After 3 weeks aging at pH 13.5 at 25°C

Stability of nanoparticle = f(solution acidity), reversible phenomena

Anisotropic Nanoparticles

Precipitation of $Al(NO_3)_3$: γ-AlO(OH) boehmite



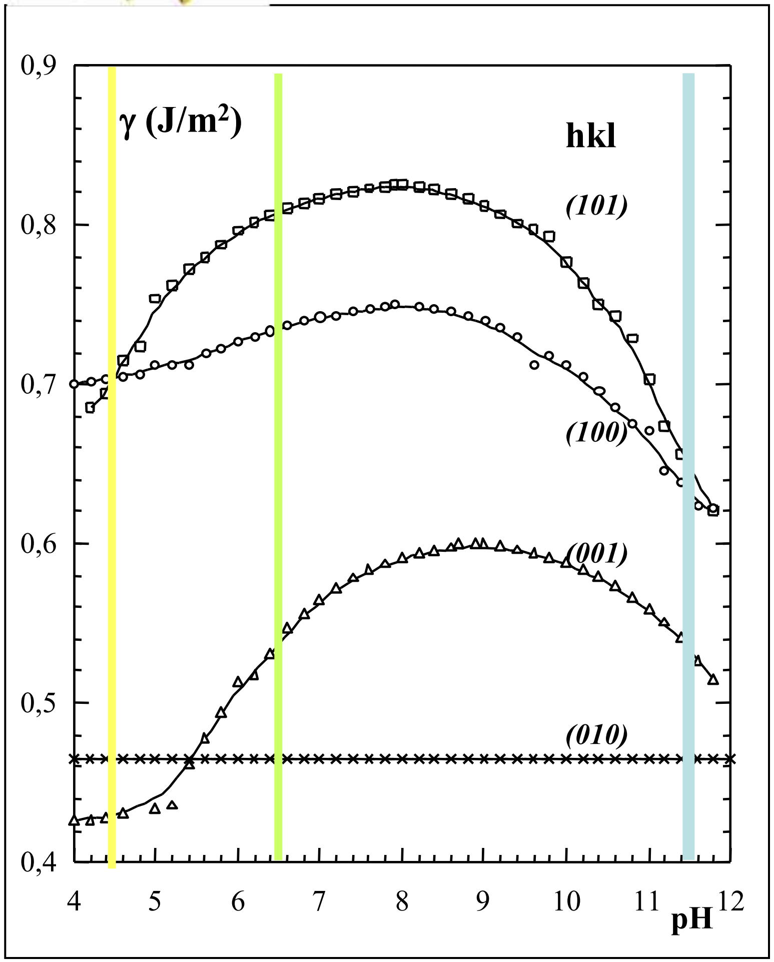


Wulff construction :
Equilibrium crystal = faces of lesser energy

Morphology
= f(Surface Energy of each face)

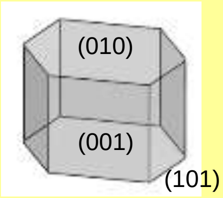
Handbook of Porous Materials, Ed. F. Schüth, Wiley-VCH, 2002, p. 1591 & J. Mater. Chem., 2004, 14, 1-9

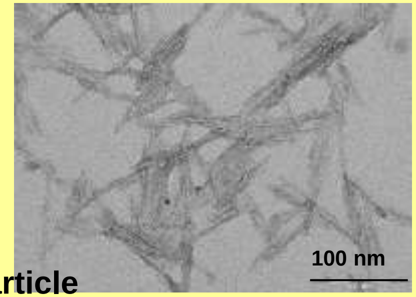
Precipitation of $Al(NO_3)_3$: γ-AlO(OH) boehmite



pH = 4.5

L= 4,5 nm
e = 3.7 nm

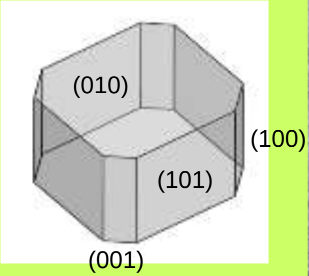


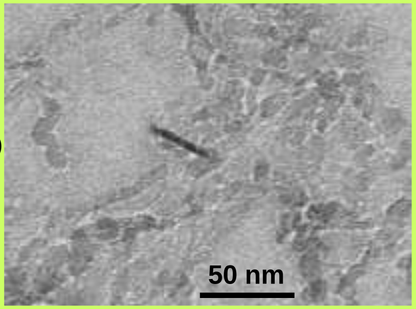


small aggregated pseudo-isotropic particle

pH = 6.5

L= 8 ± 1 nm
e = 3.7 nm

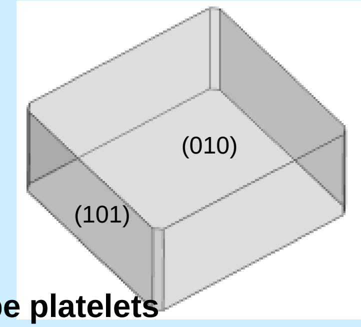


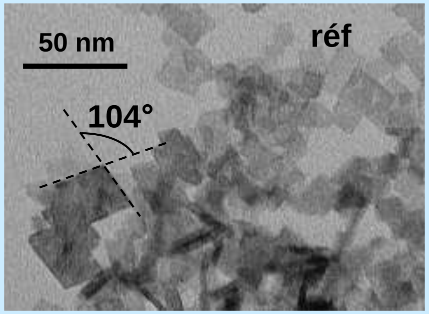


pseudo-hexagonal platelets

pH = 11.5

L= 13 ± 4 nm
e = 4.9 nm



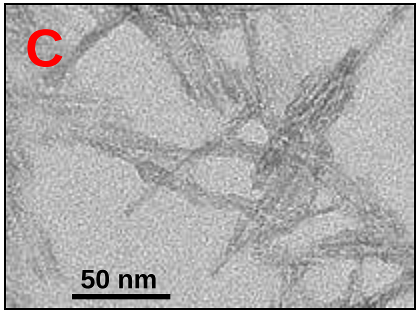


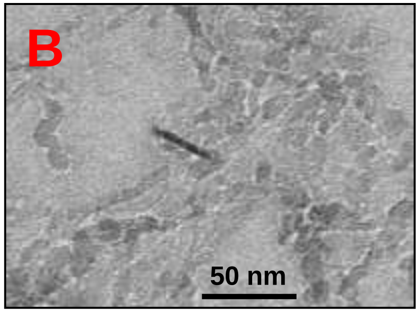
diamond shape platelets

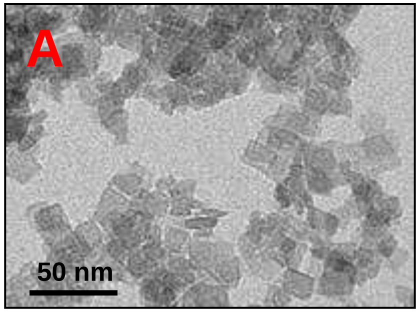
Handbook of Porous Materials, Ed. F. Schüth, Wiley-VCH, 2002, p. 1591 & J. Mater. Chem., 2004, 14, 1-9

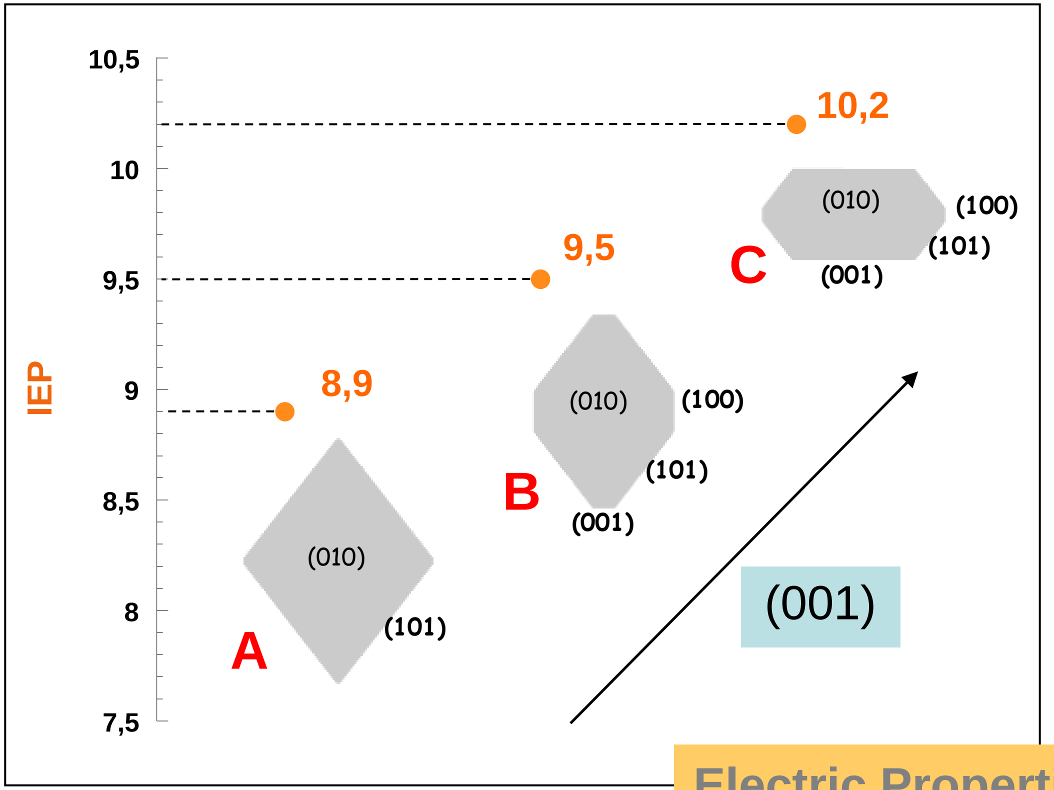
Anisotropic Nanoparticles

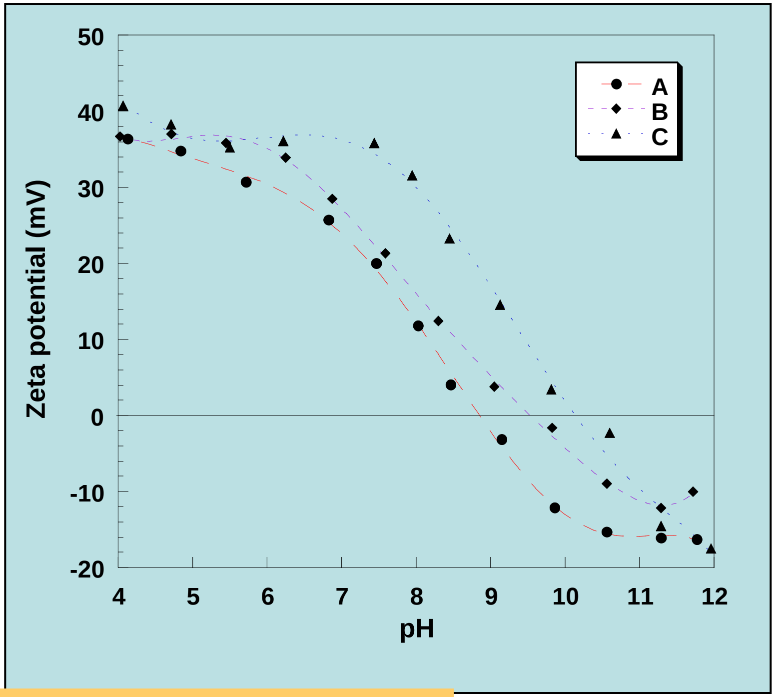
Precipitation of $Al(NO_3)_3$: γ-AlO(OH) boehmite





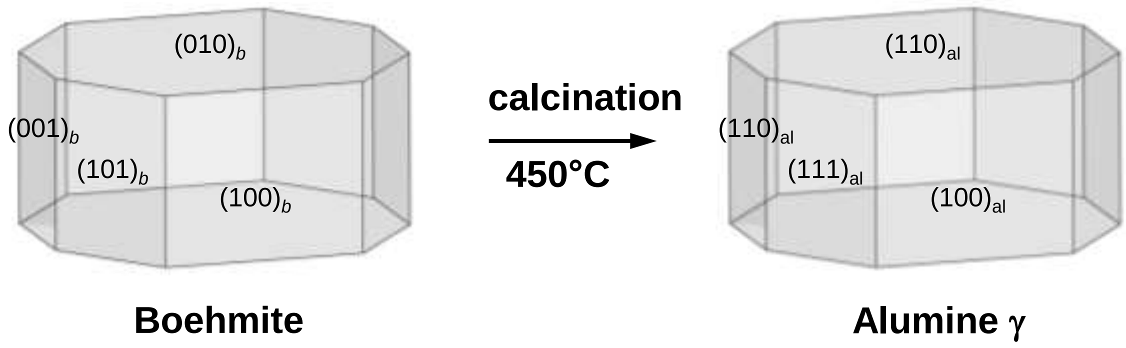


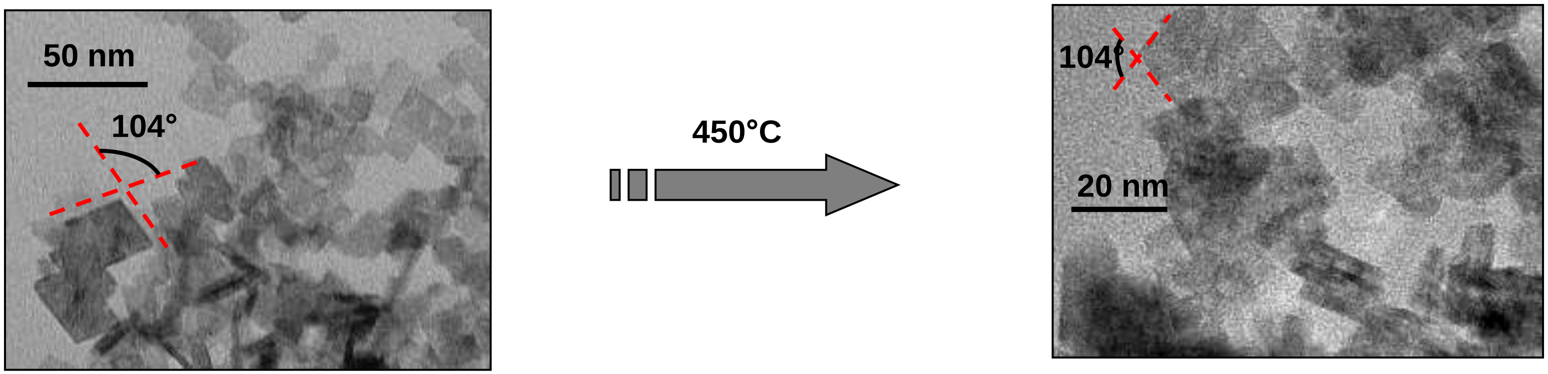




Electric Properties = f(Morphology)

Boehmite ➝ Gama Alumina : **topotactic transformation**





↪ **Morphology is kept after the heat treatment**

Euzen, P., et al., *Handbook of Porous Solids*, Wiley-VCH Verlag GmbH, 2002, Vol. 3, 1591-1676

Complexing molecules and growth of cristallites

Precipitation of $Al(NO_3)_3$ with polyols: γ-AlO(OH) boehmite

[polyol]=0.007M

Polyols

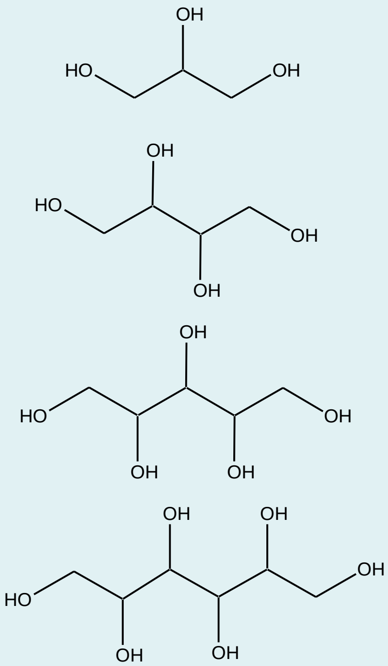
C2

C3

C4

C5

C6

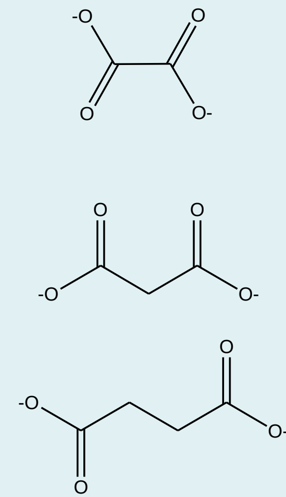


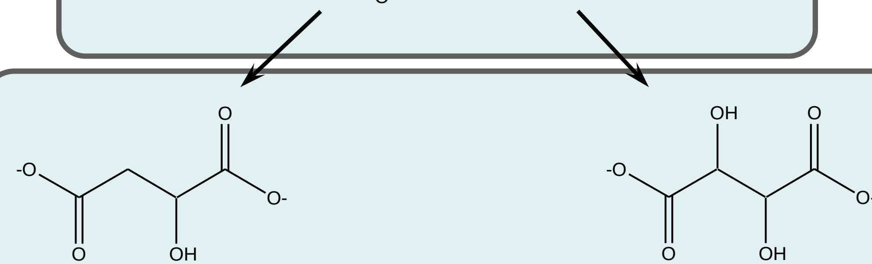
Dicarboxylates

C2

C3

C4

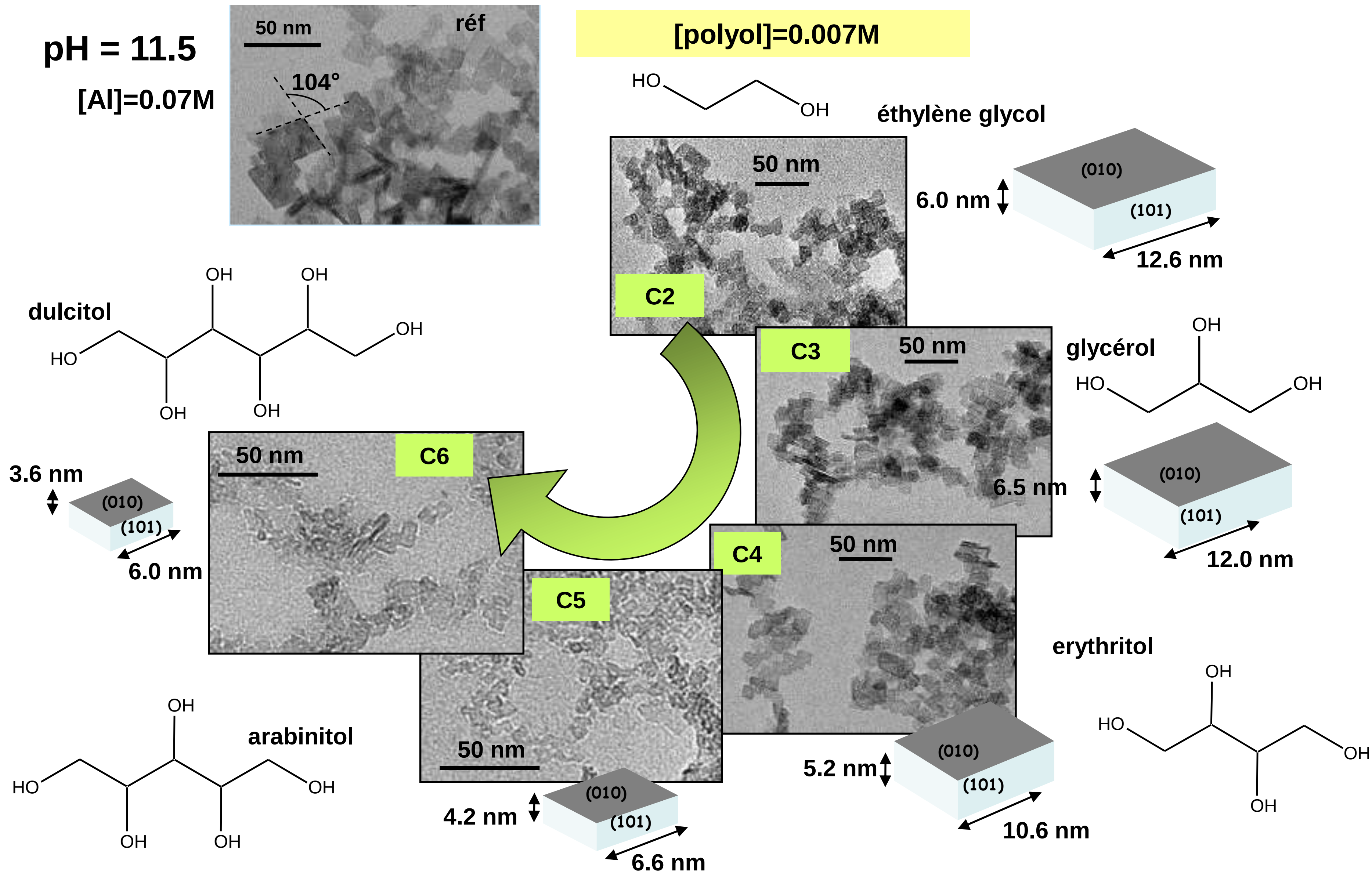




Hydroxycarboxylates

Surface complexation by polyols

Precipitation of $Al(NO_3)_3$ with polyols: γ-AlO(OH) boehmite



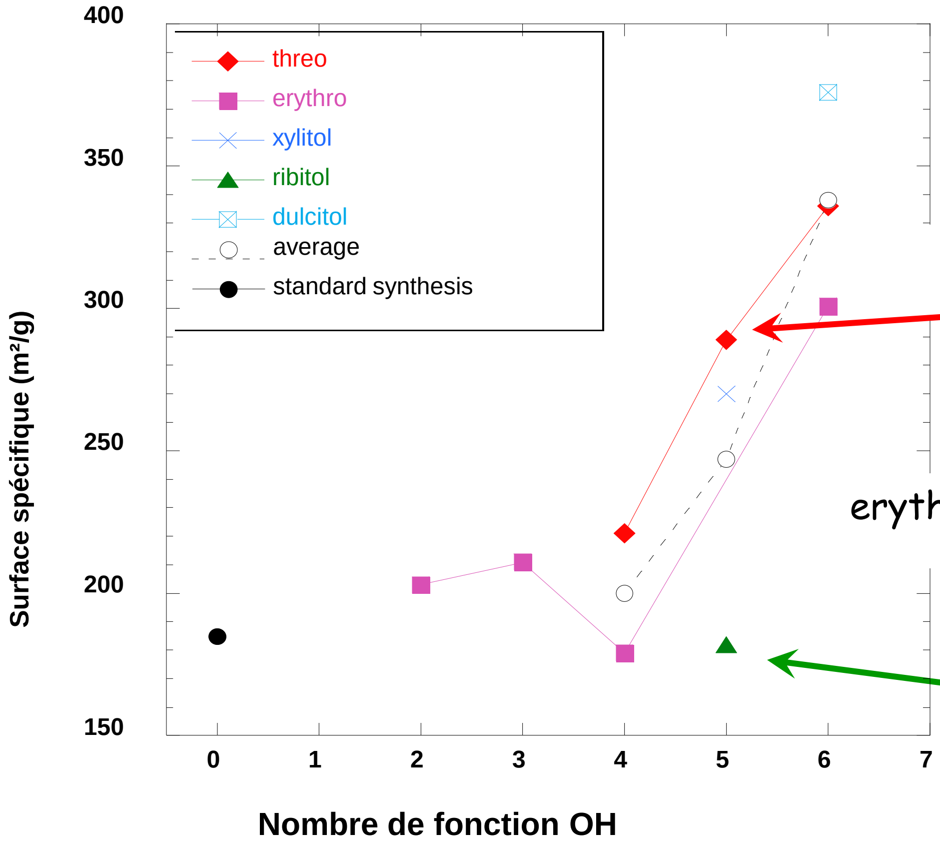
The size of nanoparticles decreases with the length of polyols

Surface complexation by polyols

Precipitation of $Al(NO_3)_3$ with polyols: γ-AlO(OH) boehmite

[polyol] 10 % mol

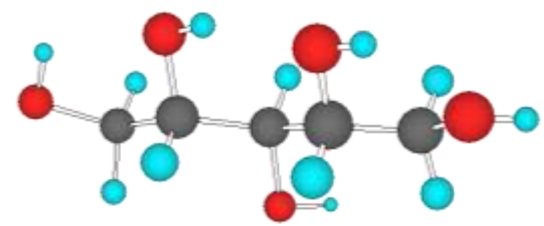
Xylitol : 290 m^2/g



threo

erythro

Stereochemistry effect

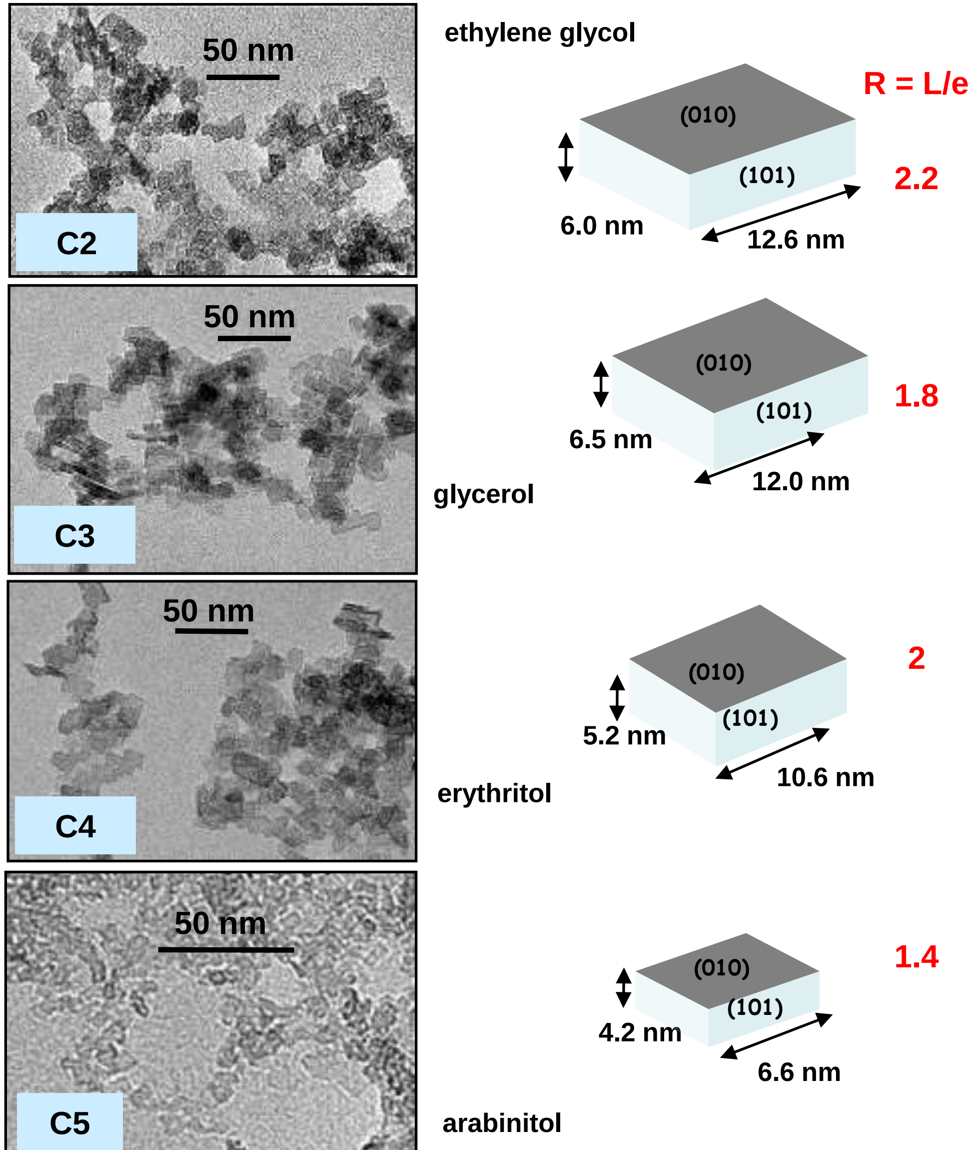


Ribitol : 180 m^2/g

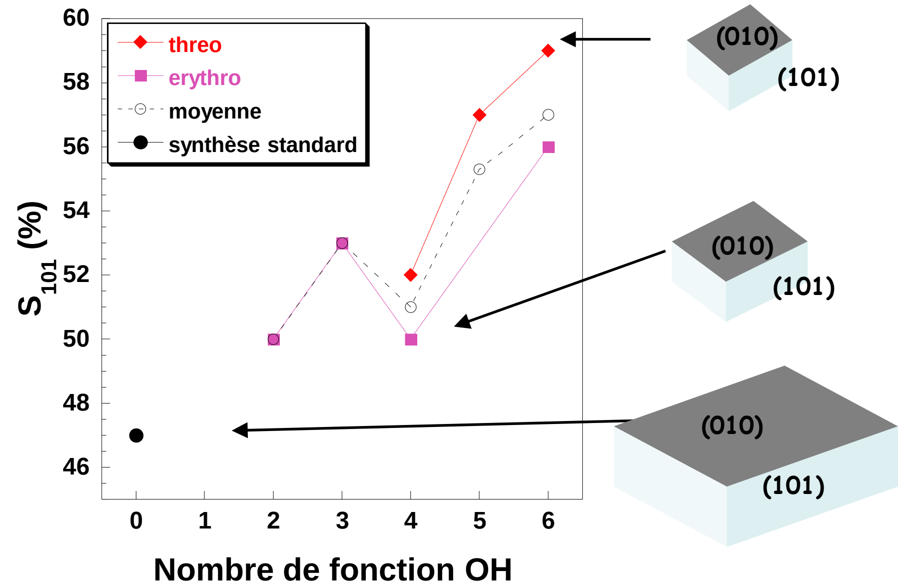
Chiche D. (2007), Thesis UPMC- IFP, Paris 6
Heterogenous Catalysts, Elsevier, 2006, 393

Surface complexation by polyols

Precipitation of $Al(NO_3)_3$ with polyols: γ-AlO(OH) boehmite



Stabilisation énergétique des faces (101)

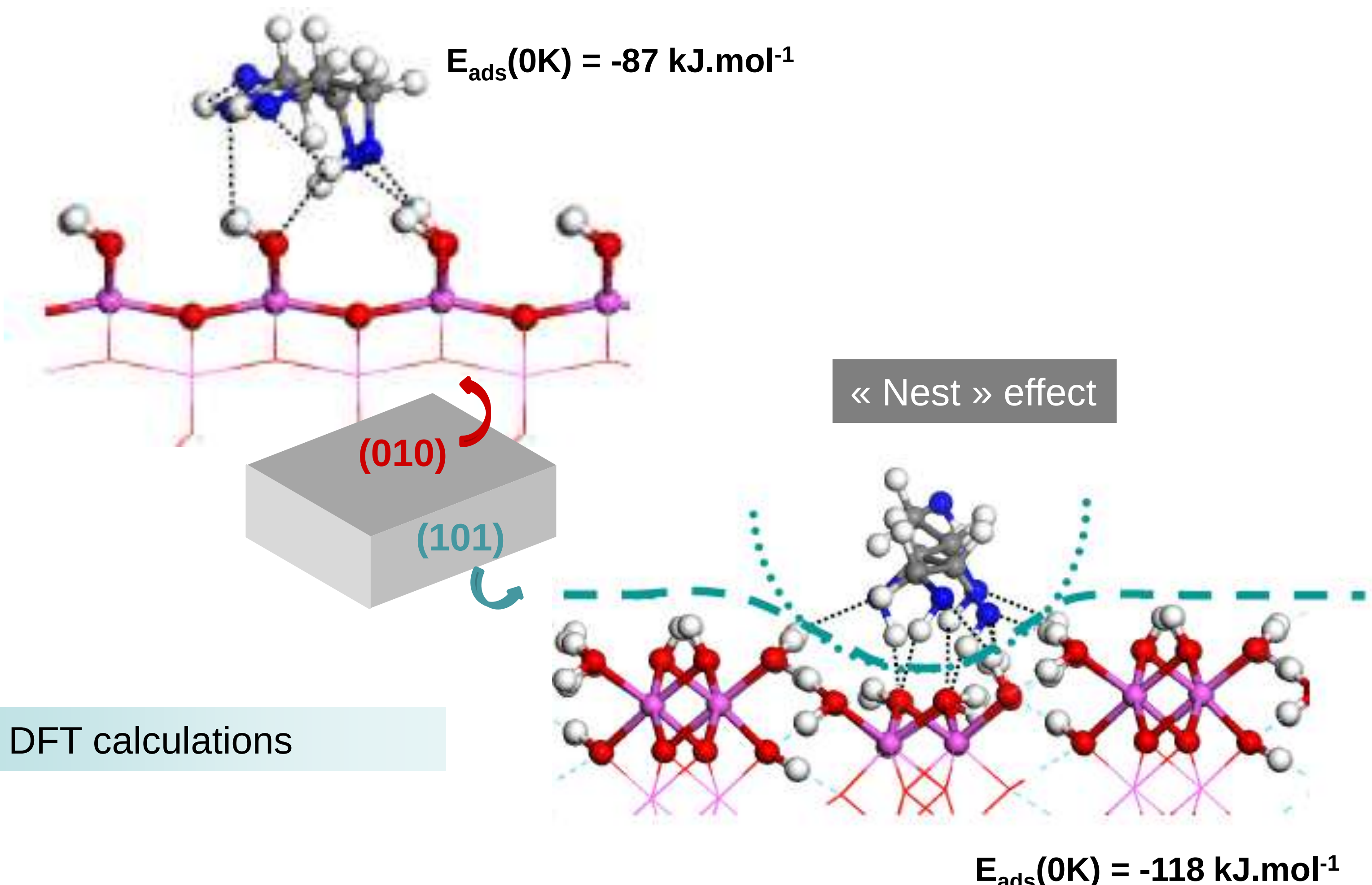


Aspect ratio evolution :
Preferential adsorption upon lateral surfaces

Specific adsorption of Polyols on (101) face: Selectivity of adsorbed species

Phys. Chem. Chem. Phys., 2009, 11, 11310 - 11323

Surface complexation by polyols



DFT calculations

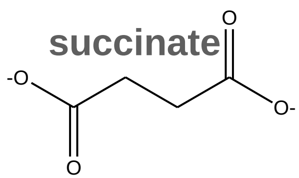
Preferential adsorption upon
lateral surfaces : concavitie and stabilisation

Phys. Chem. Chem. Phys., 2009, 11, 11310 - 11323

Surface complexation by hydroxy carboxylate

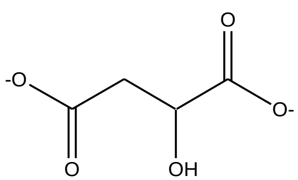
poly(hydroxy)carboxylates 0.007M

succinate **2,2**

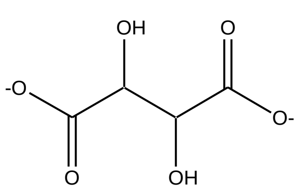


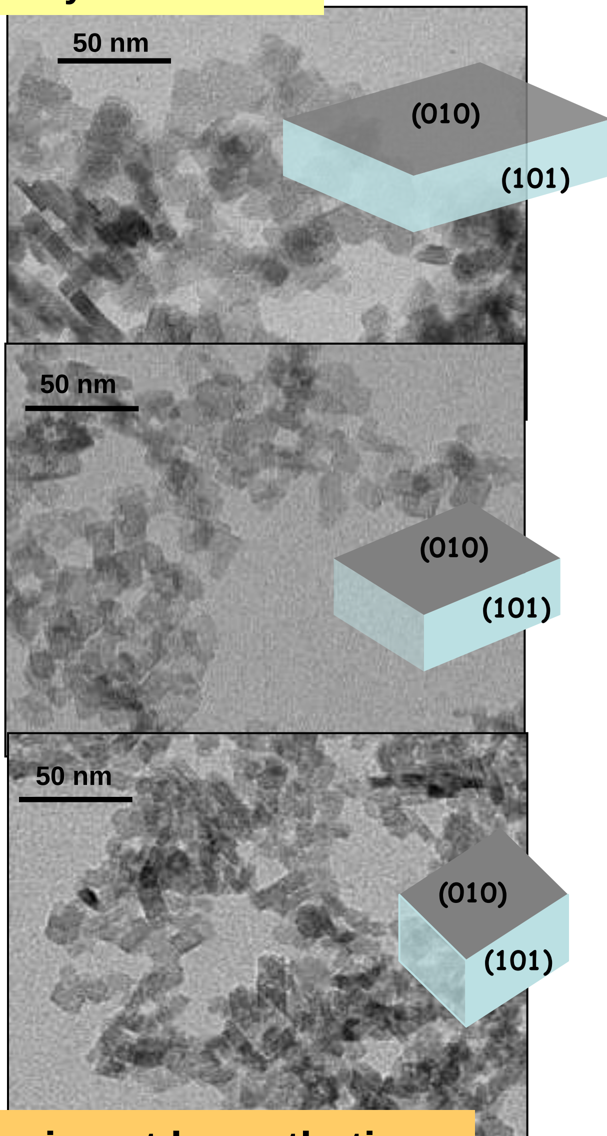
R = l/e

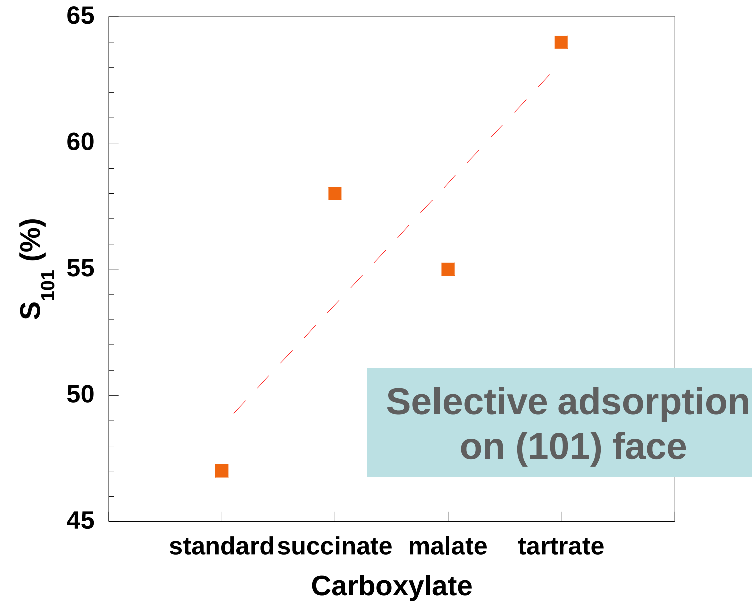
malate **1,6**



tartrate **1,1**

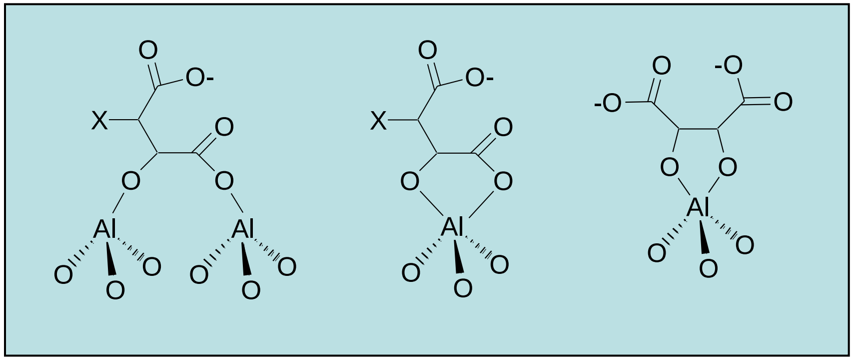






Hydroxy carboxylate chemisorption

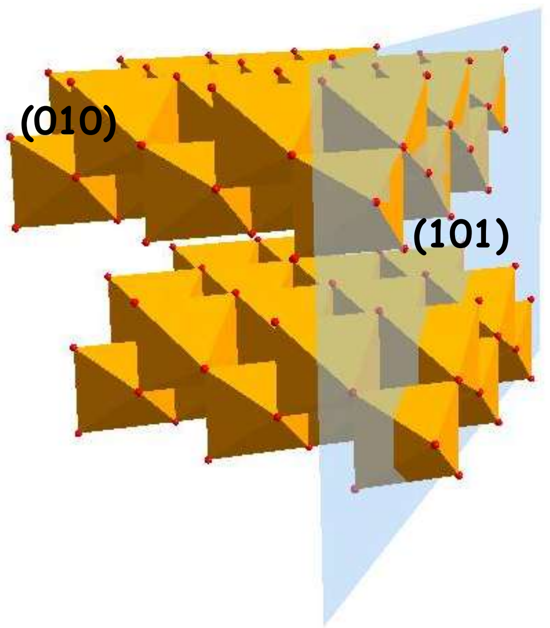
Geffroy 1999, Haines 1974, Martell 1984

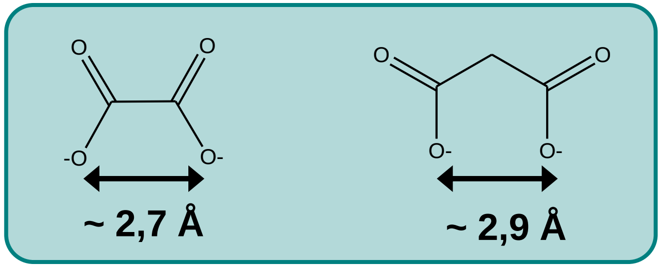


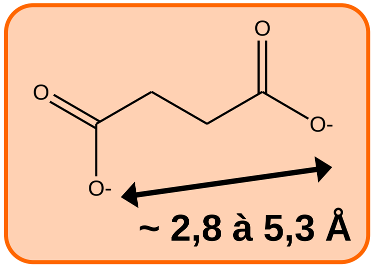
Size variation is not homothetic : Strong decrease of anisotropy

Acidity of OH groups is strengthened by the complexation

Surface complexation by hydroxy carboxylate







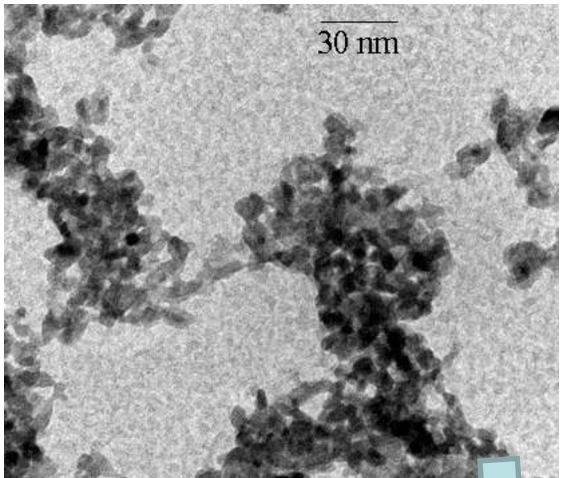
(101)	D(O-O) (Å)
μ_1-OH / μ_1-OH	2,7 - 4,0 - 4,7 - 6,3
μ_2-OH / μ_2-OH	2,5 - 4,7 - 5,5 - 6,3
μ_1-OH / μ_2-OH	2,5 - 2,8 - 3,8 - 4,9 - 5,3 - 5,7

Lower reactivity of (010) face due to μ_2-OH sites.

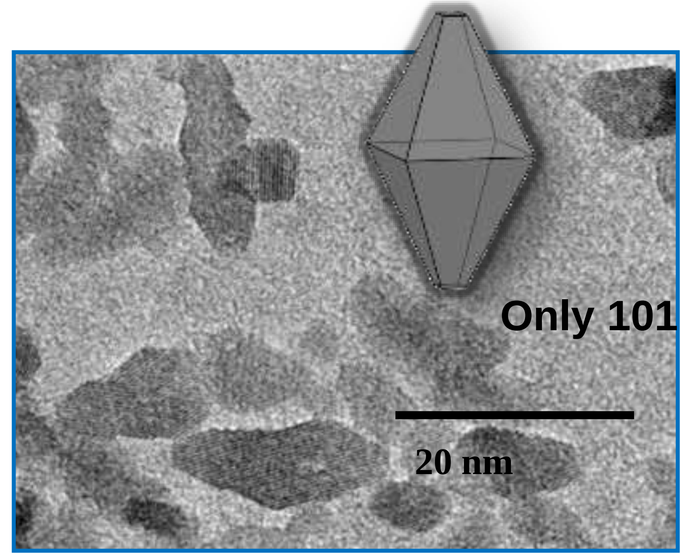
Increase of (101) face stabilization with the distance between –COOH groups: more available adsorption sites.

Surface complexation and shape of anatase nanoparticles

Anatase nanoparticles obtained without complexant



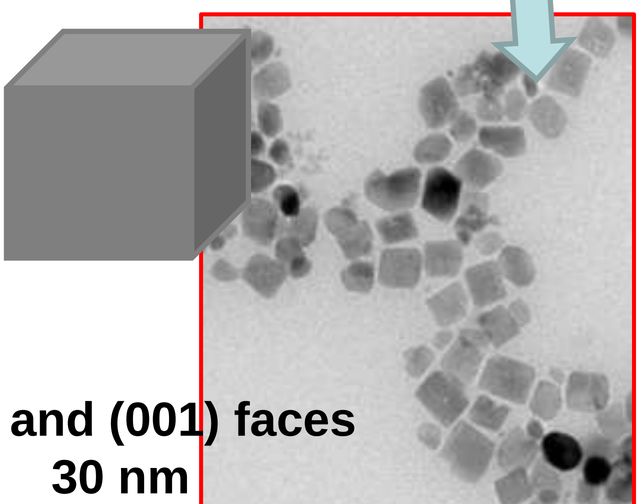
In presence of glutamic acid



Only 101 faces

Durupthy, O.; Bill, J.; Aldinger, F. Cryst. Growth Des. ***2007****, 7, 2696*

In presence of oleic acid

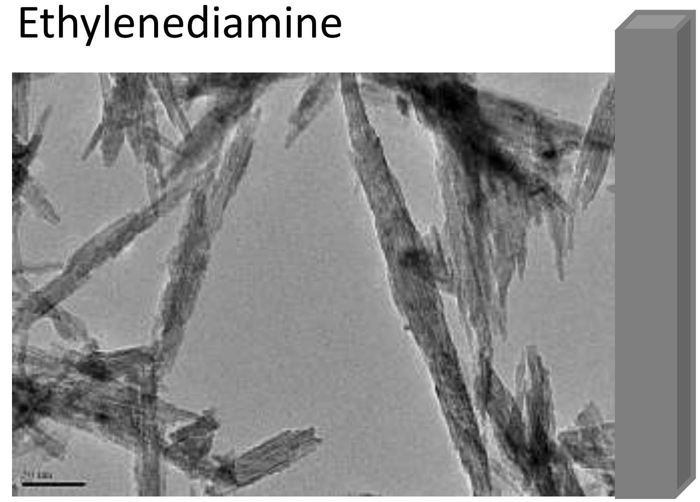


(100) and (001) faces

30 nm

Matijevic, J. Colloid Interface Sci. 103 (1985)

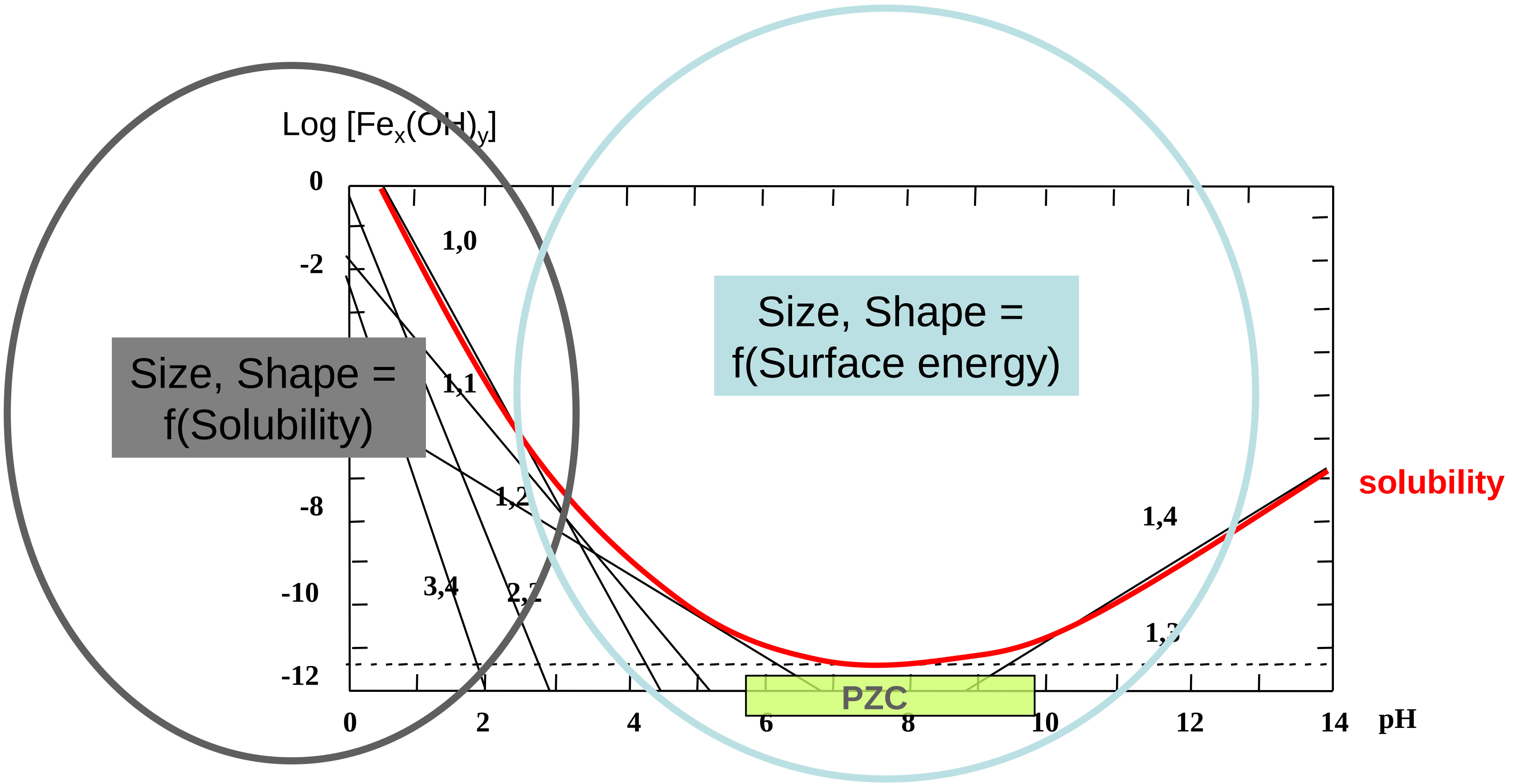
Ethylenediamine



(100) faces

Sugimoto, T.; Zhou, X. P.; Muramatsu, A. *Journal of Colloid and Interface Science* **2003**, *259*, 53

What are the relevant parameters to control the growth of nanoparticles ?

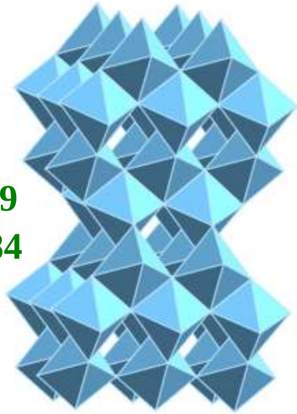
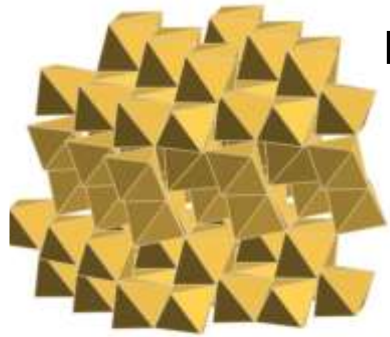
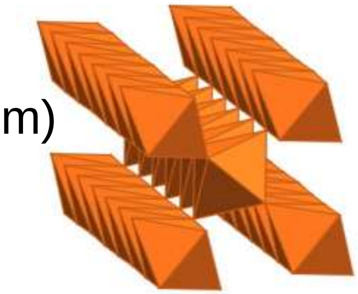


Titanium oxide Nanoparticles

Pigment : paints, papers, plastics, cosmetic and pharmacy
Photocatalysis, photovoltaic …

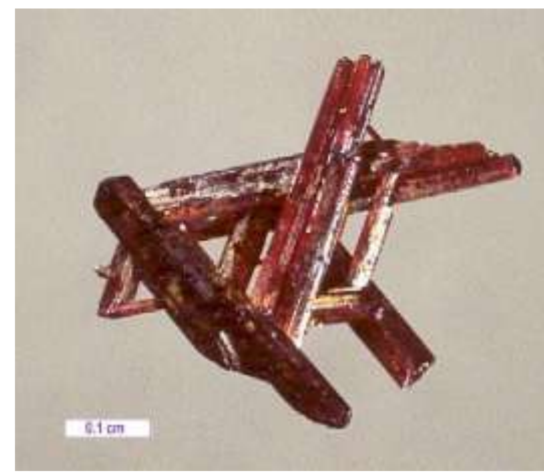
3 polymorphs

	Anatase ($I4_1/amd$)	Brookite ($Pcab$)	Rutile ($P4_2/mnm$)
ΔH°f ($kJ.mol^{-1}$)	-939	-941	-944
ρ (g/cm^{-3})	3,84	4,17	4,26


Mine Falls Park, Nashua, NH


Mina Maria,Caneca, Sonora, Mexico

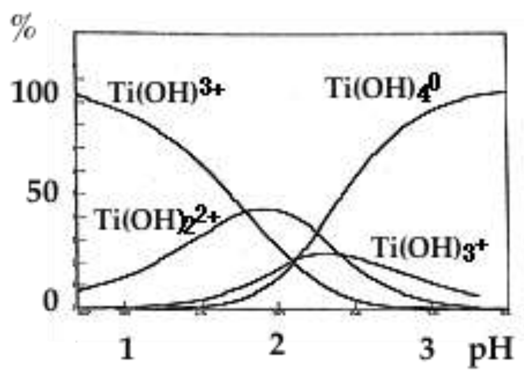

Stony Point, Alexander County, NC

Cristalline structure depends on synthesis conditions

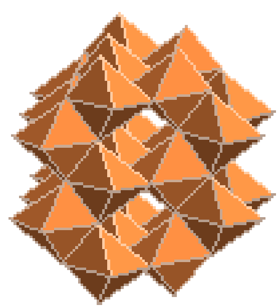
Titanium oxide Nanoparticles

$[Ti(OH)_4(OH_2)_2]^0$ —Olation / Oxolation→ TiO_2

Alcalinisation
2 ≤ pH ≤ 6

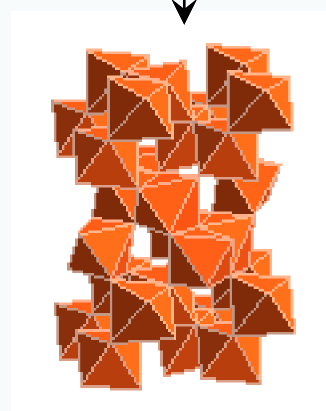


$Ti(OH)_4(OH_2)_2{}^0$



TiO_2 anatase

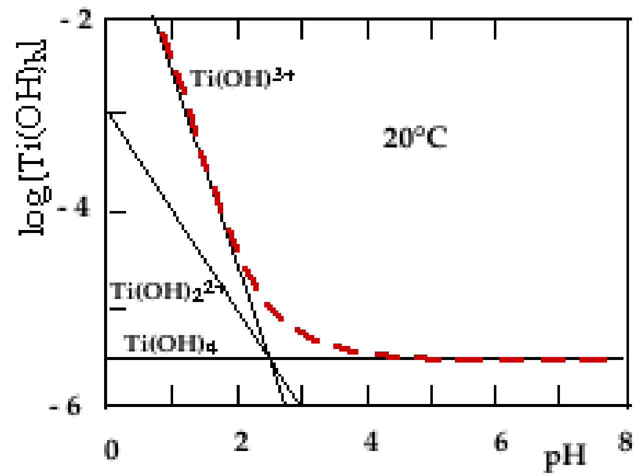
$Ti(OH)_2X_2(OH_2)_2{}^0$

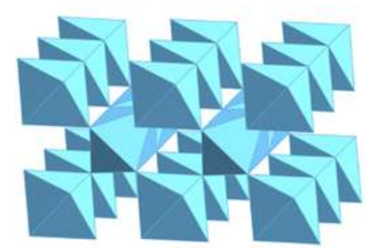


brookite

Thermolysis with chlorides

Thermolysis in acidic medium
$Ti(OH)_2(OH_2)_4{}^{2+}$
≈ 100°C





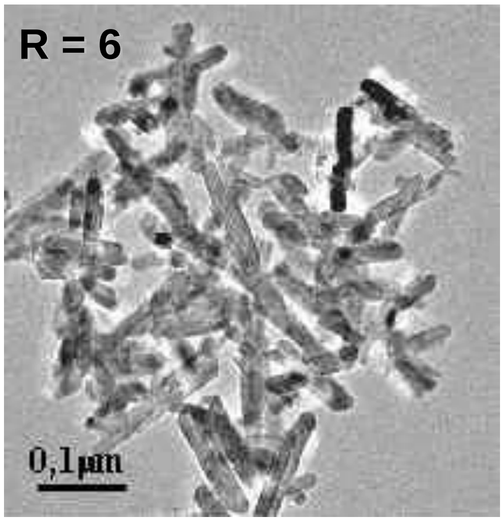
rutile

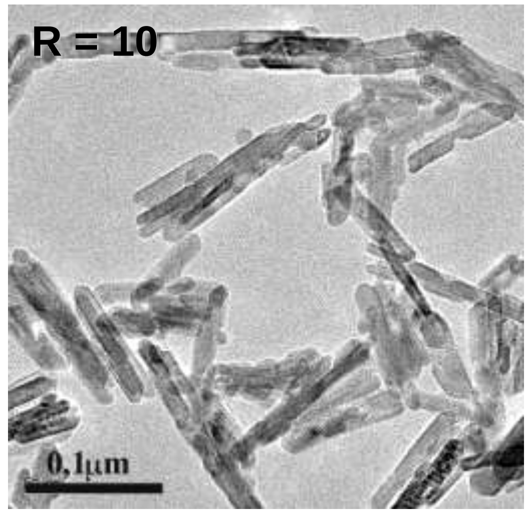
Titanium oxide Nanoparticles

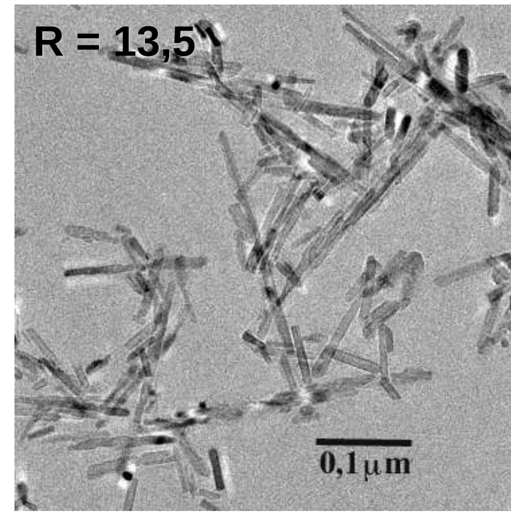
Thermolysis of $TiCl_4$: TiO_2 rutile

Weak nucleation : slow precipitation
High solubility : favour the growth

$$R = \frac{\text{length}}{\text{wide}}$$



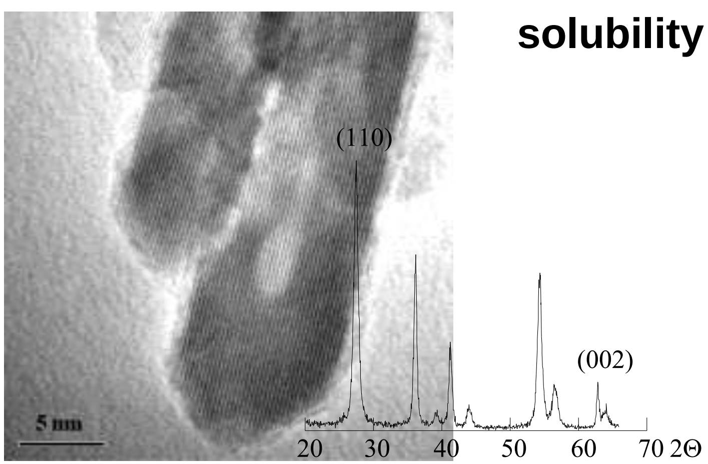


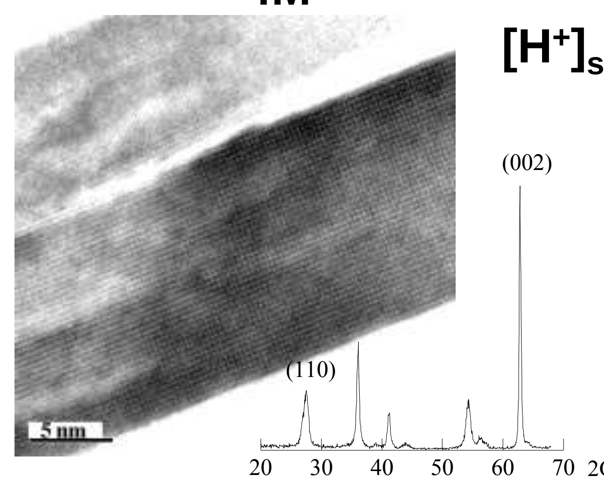


1 M → **2 M** → **4M** →

solubility increase

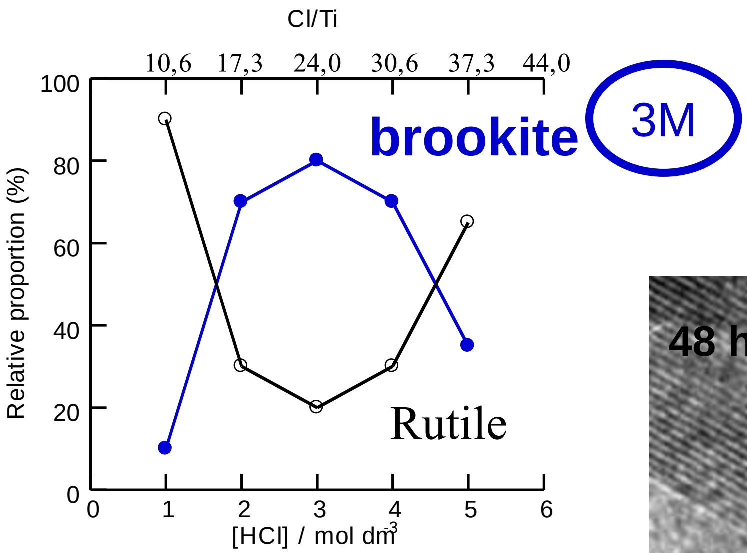
$[H^+]_{sol}$





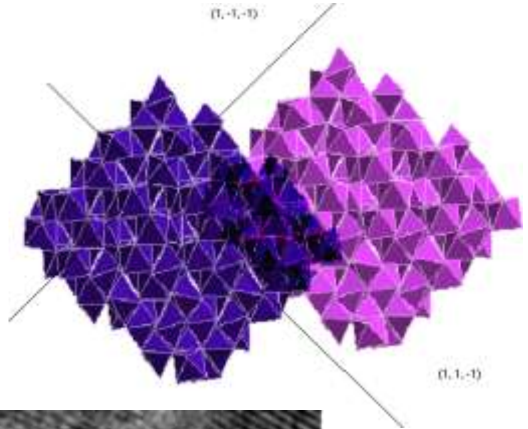
Thermolysis of $TiCl_4$ with chloride : TiO_2 brookite

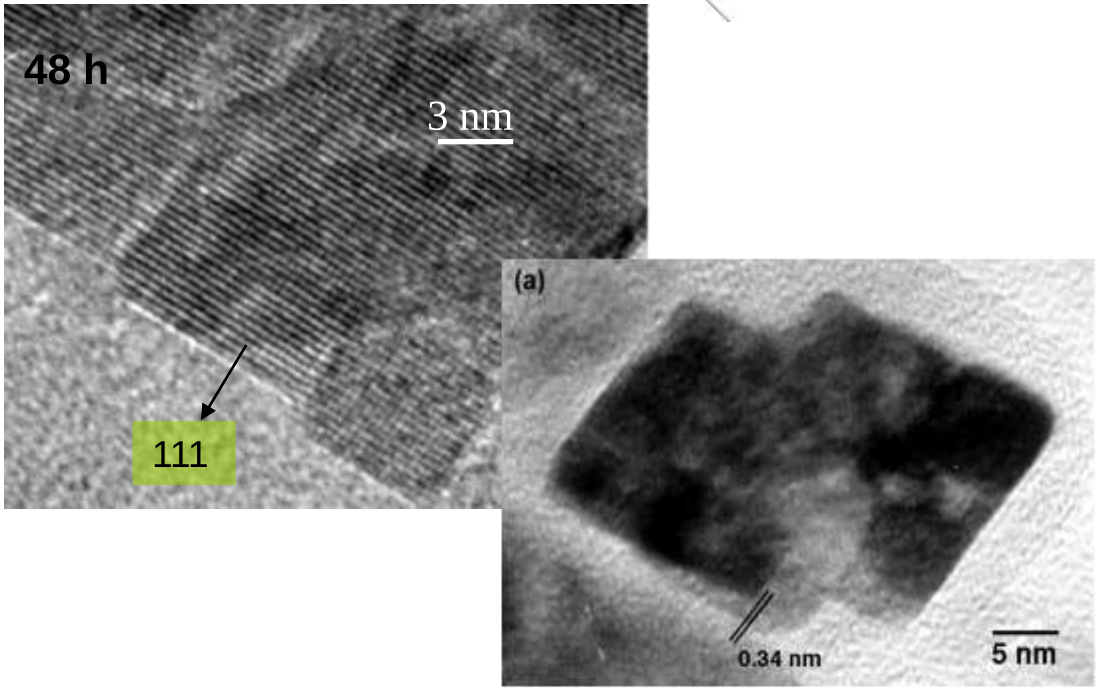
$TiCl_4$ 0,15 M / HCl / 95°C 48 hours



17 <Cl/Ti <35

$[Ti(OH)_2Cl_2(H_2O)_2]^0$

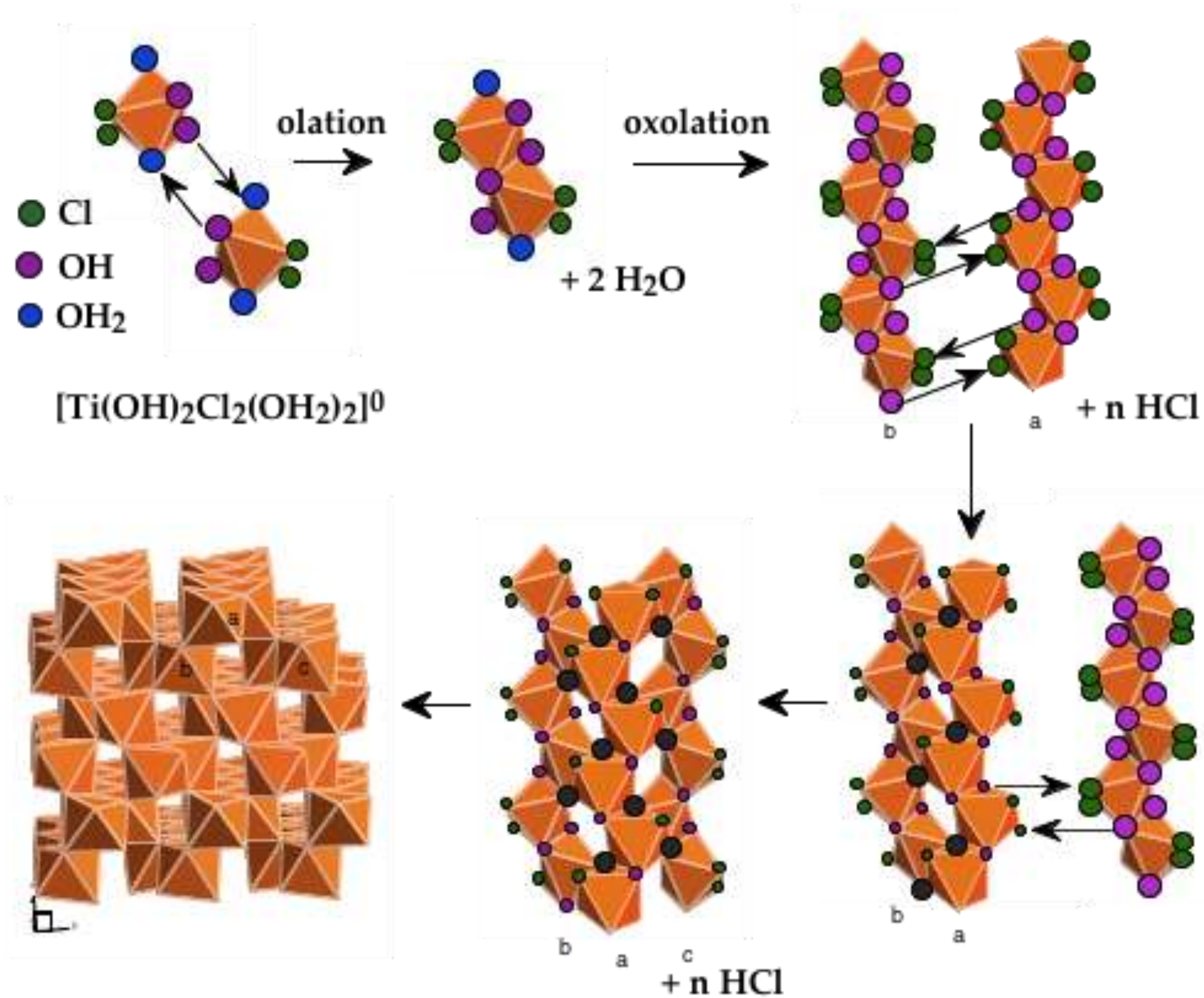




A. Pottier, S. Cassaignon, C. Chaneac , F. Vilain, E. Tronc, J.P. Jolivet, J. Mater. Chem., 13, 877 (2003)

Titanium oxide Nanoparticles

Thermolysis of $TiCl_4$ with chloride : TiO_2 brookite

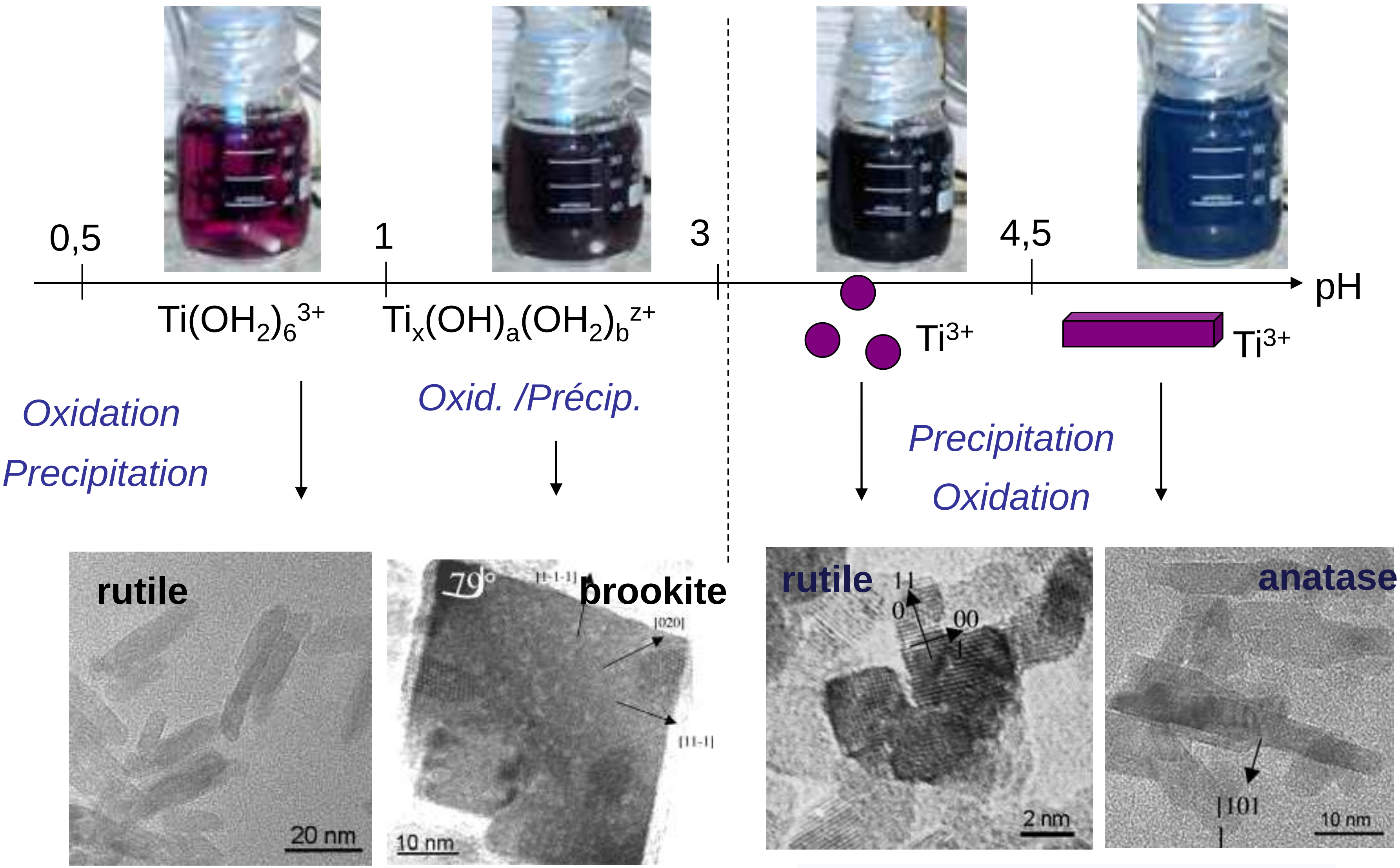


Structure control by a complexing agent

A. Pottier et al. J. Chem. Mater. 2001, 11, 1116

Titanium oxide Nanoparticles

Hydrolysis of Ti(III)



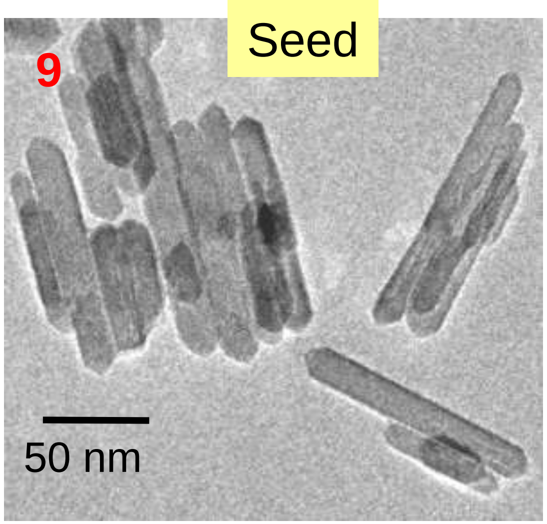
New Morphologies for TiO_2

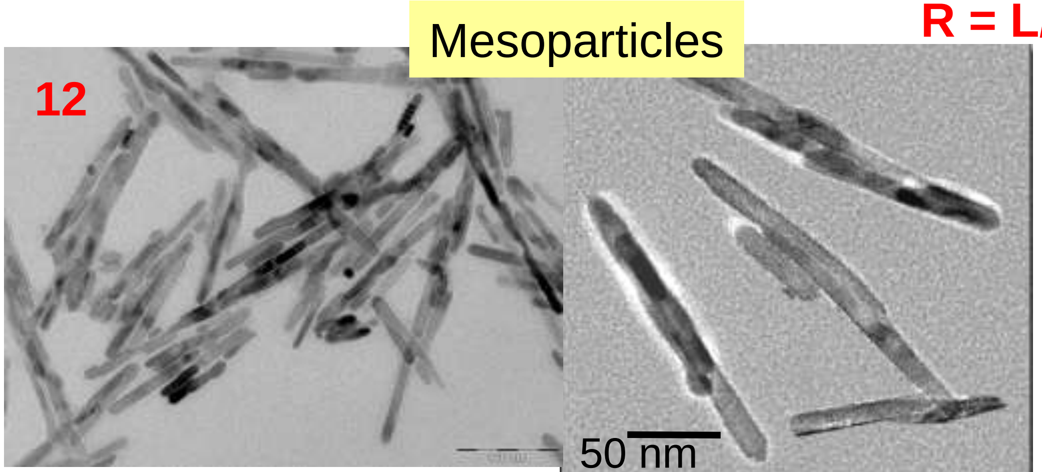
S. Cassaignon et al., J. Phys. Chem. Solids (2007), doi:10.1016

Growth control and Seeding

TiO_2 Rutile : $TiCl_4$ 3 M / HNO_3 15M / 120°C 24 hours

Q. Huang, L. Gao, Chem. Letters, 2003, 32,7

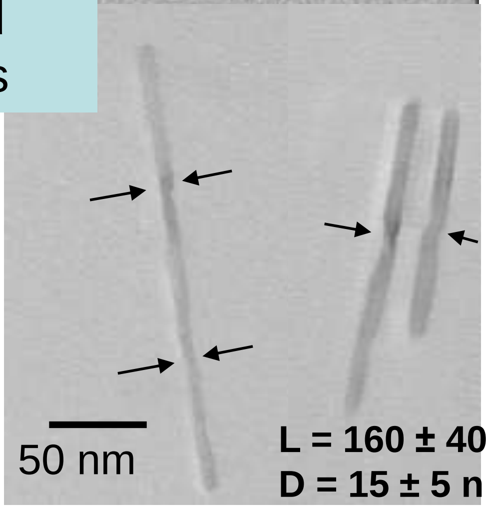




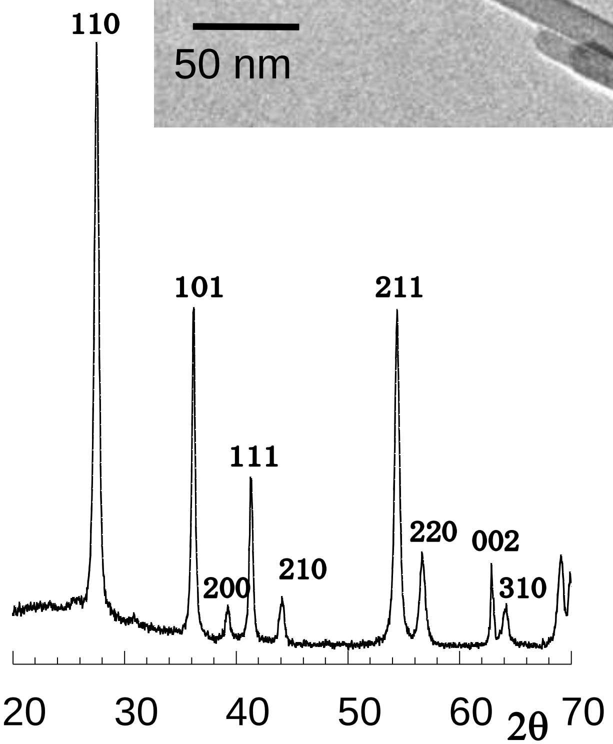
R = L/l

seed-mediated growth process

+ Growth solution : $C(Ti^{4+})$=0,3M



L = 160 ± 40 nm
D = 15 ± 5 nm



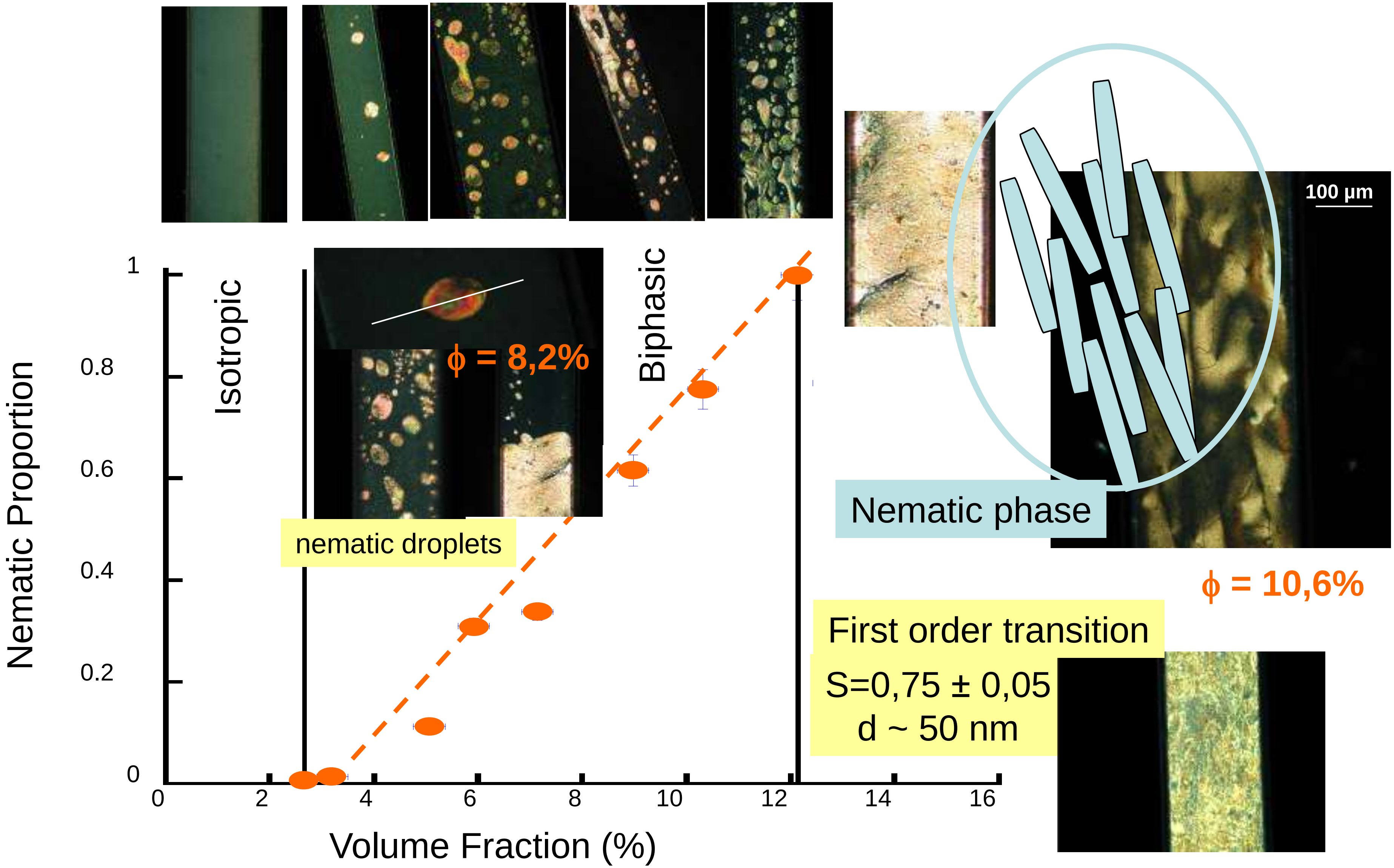
Dessombz A.,Thesis UPMC-Orsay,Paris 11

Volume fraction : f = 13,3%

***JACS**, 2007,129 (18),5904*

Properties of long nanorods

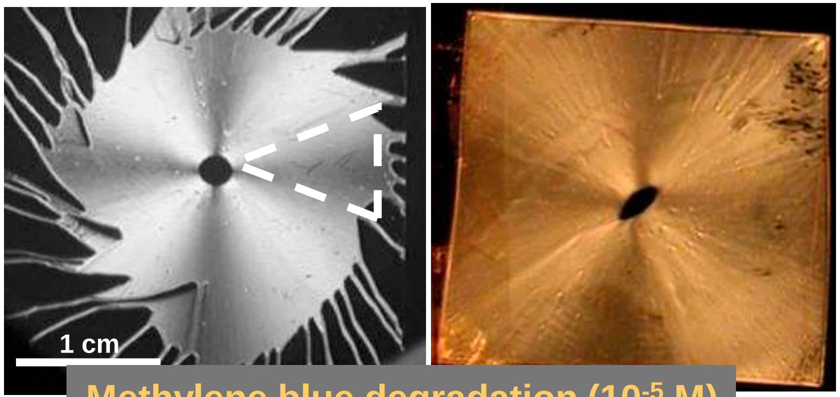
Collaboration : Patrick Davidson, **LPS Orsay,** Pierre Panine, **ESRF Grenoble**



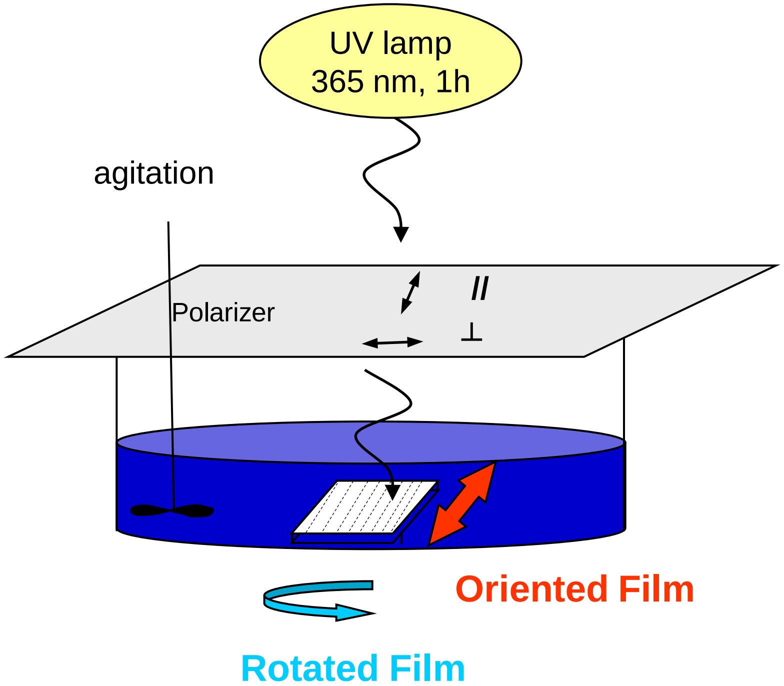
Dessombz A.,Thesis UPMC-Orsay, Paris 11

***JACS**, 2007,129 (18),5904*

Properties of long nanorods

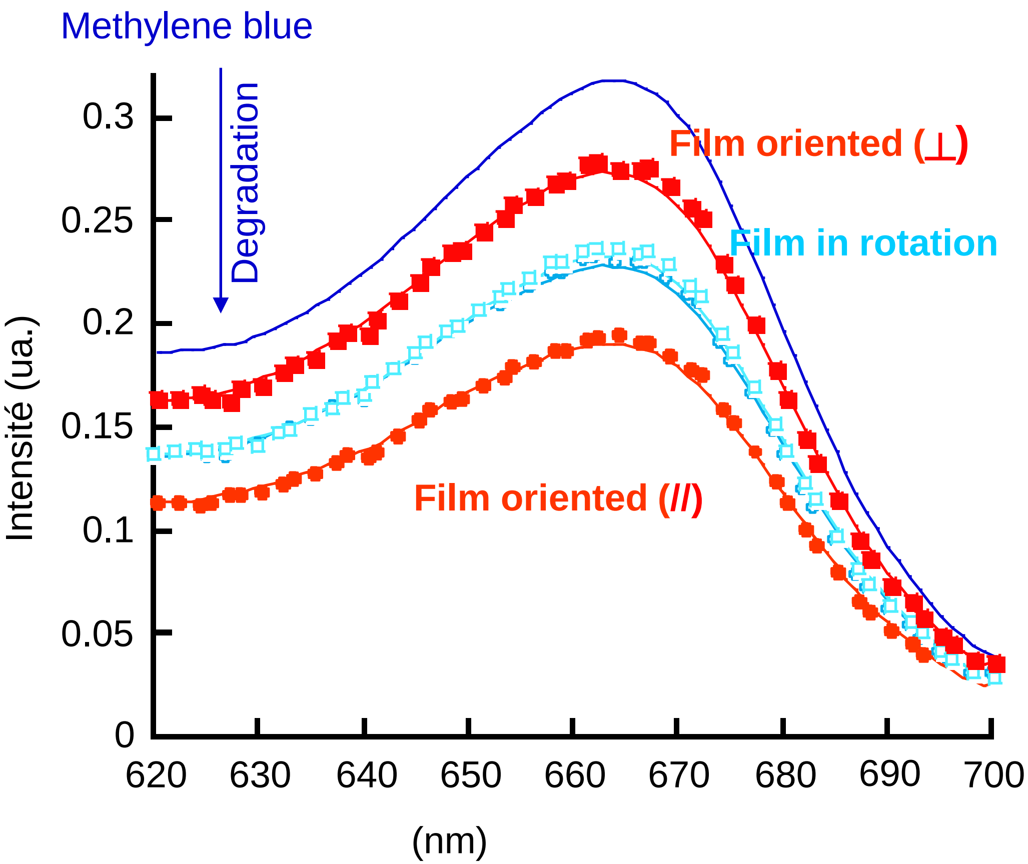


Methylene blue degradation (10^{-5} M)



Photocatalysis study

Dessombz A.,Thesis UPMC-Orsay,Paris 11

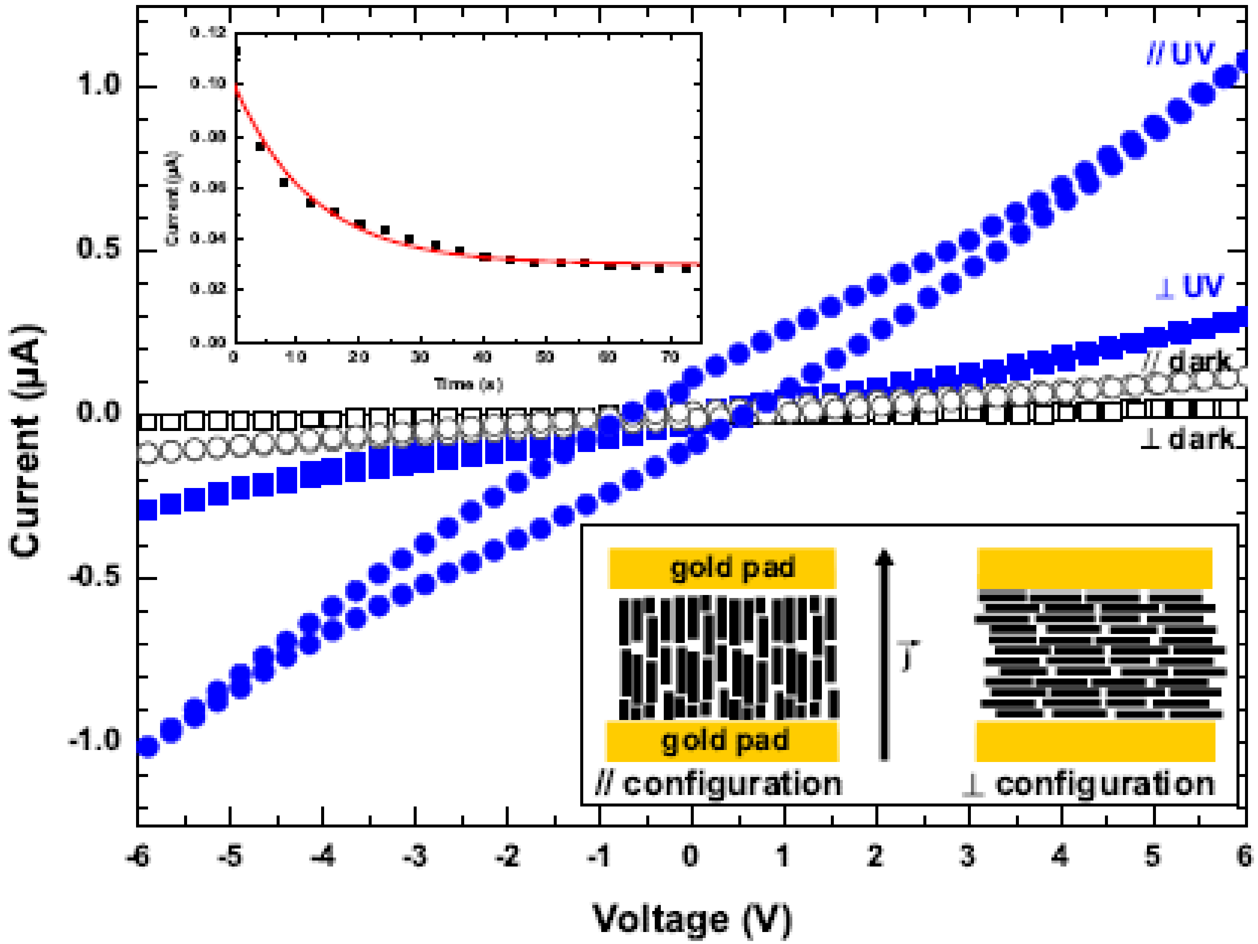


Oriented aggregation: Increase of the photocatalytic activity

***JACS**, 2007,129 (18),5904*

Collaboration : Patrick Davidson, **LPS Orsay,** Pierre Panine, **ESRF Grenoble**

Properties of long nanorods



Anisotropy of electric properties; Photoactivation of current

Conclusion

- Aqueous chemistry of metal cations: environmentally friendly, Low cost

- Versatile way to tune oxide nanoparticles

  Size, shape and crystalline structure

- Identification of relevant synthesis parameters to tune size and shape:

  pH and acidity,
  used of polyfunctionnal complexant : Polyols, Polycarboxylates

Surface energy and solubility of nanoparticles are the driving force of their evolution

Acknowledgements

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Elisabeth Tronc, CR




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Agnès Pottier, Cédric Froidefond, Micaëla Nazaraly
Yuheng Wang, Anne Carton, Roberta Brayner, Pierre Gibot (Post Doc), Christelle Roy (Master)

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Draka Comtech, Marcoussis
Saint – Gobain Research, Aubervilliers
Lhoist, Belgium

University Pierre et Marie Curie, Paris, France

Jean-Yves Bottero, Mark Wiesner

Mélanie Auffan ,
Jérôme Rose
CEREGE

Thank you for your attention