



**Nanomateriaux-Nanocristallinité- Supracristal**

<http://www.supranano.fr/>

## La matière à différentes échelles

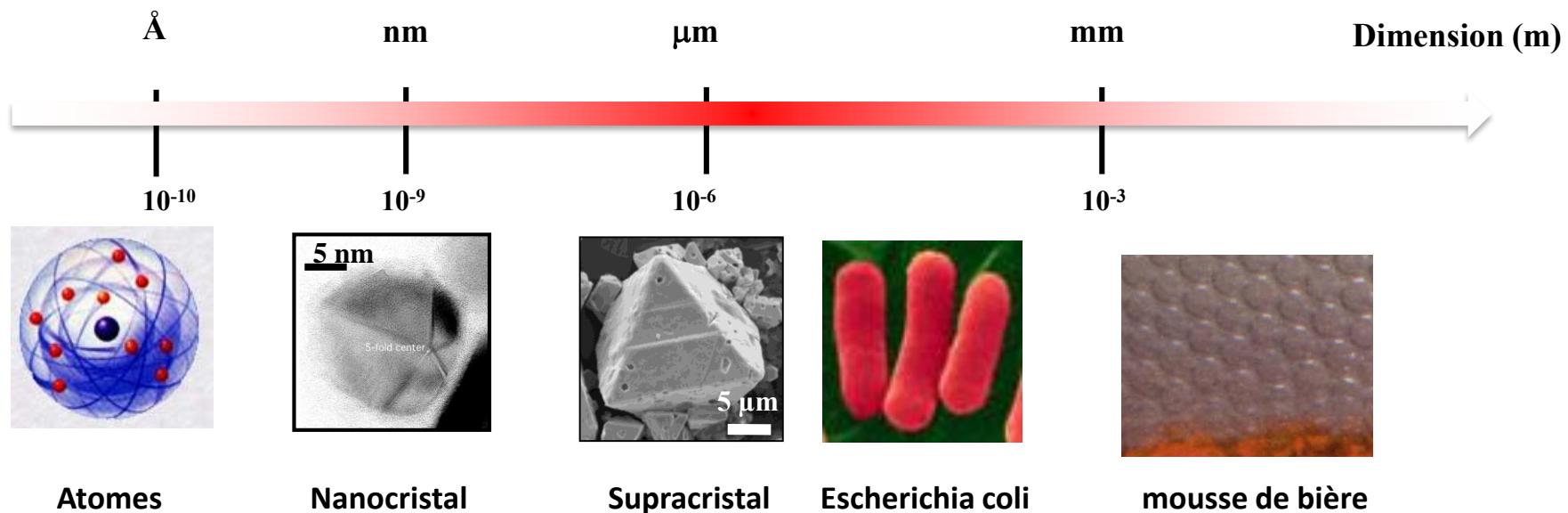
Que la Nature nous apprend-t-elle?

**Nanocristallinité: Cristallinité des nanomatériaux ( ordre des atomes dans une nanoparticule)**

**Supracristaux: assemblage cristallin à 3D de nanocristaux (ordre cristallin des nanocristaux)**

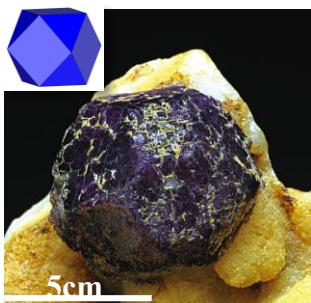
**Propriétés intrinsèques dues à l'autoassemblage cristallin de nanocristaux.**

**Analogies entre les supracristaux et les cristaux atomiques.**



# Forme des cristaux atomiques dans la Nature

Fluorite



grenat



Fluorine



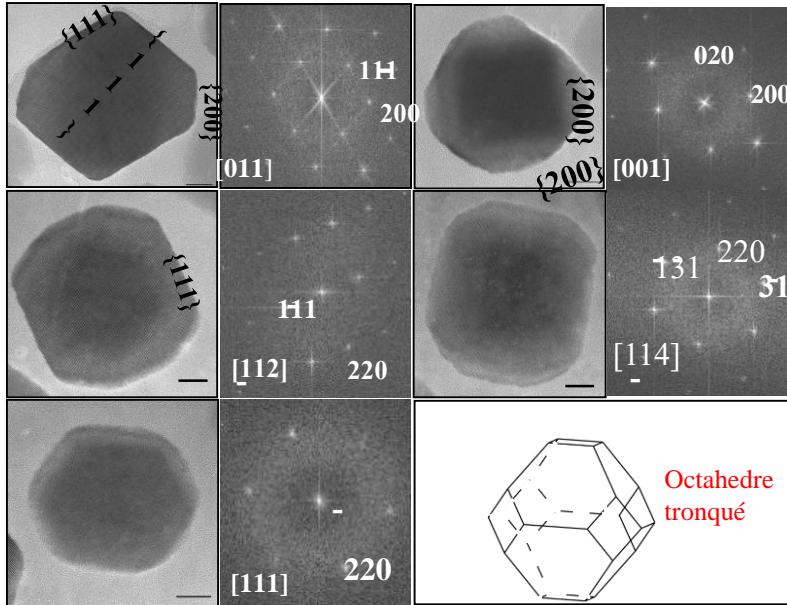
Cassiterite



Cubo-octahedre

Decahedre

## Bactérie magnetostatique



Depuis 70 millions d'années, ces bactéries sont capables de synthétiser des nanoparticules d'environ 50-nm

## La matière à différentes échelles

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Nanocristallinité: Cristallinité des nanomatériaux ( ordre des atomes dans une nanoparticule)

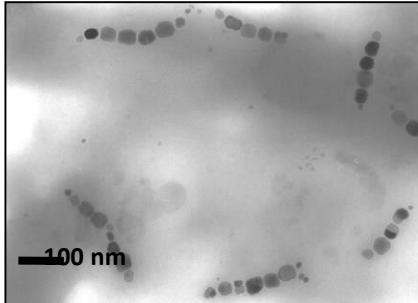
Supracristaux: assemblage cristallin à 3D de nanocristaux (ordre cristallin des nanocristaux)

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Analogies entre les supracristaux et les cristaux atomiques.

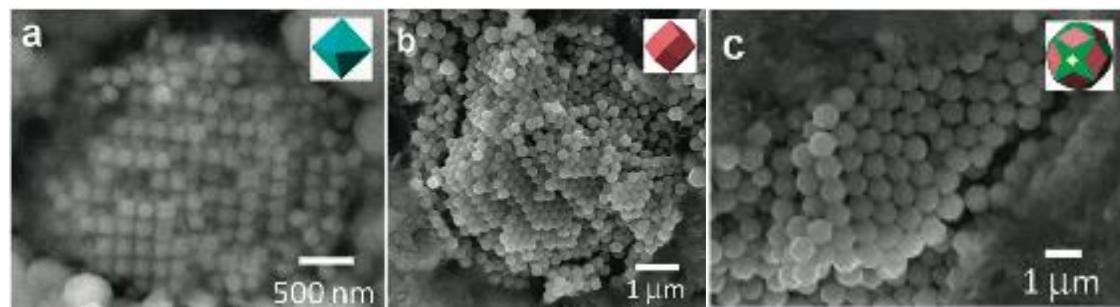
# Auto assemblage d'un seul élément (particules de $\text{Fe}_3\text{O}_4$ )

Bactérie  
Magnetostatique



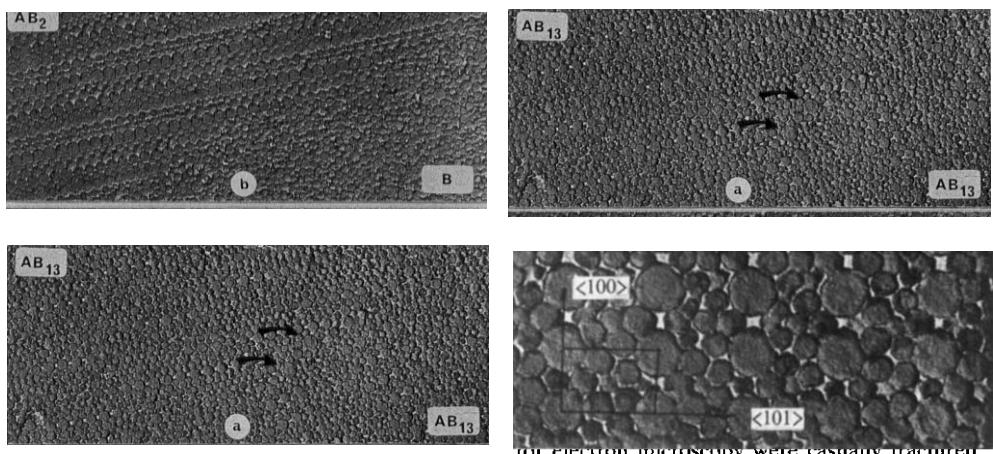
E. Alphandery, A.T. Ngo, C. Lefevre, I. Lisiecki, L.F. Wu and M.P. Pileni J. Phys. Chem. C 112, 12304-12309 (2008)

Il y a 5 milliards d'années dans le système solaire



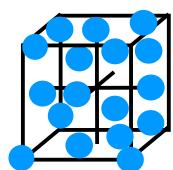
Nozawa, J.; Tsukamoto, K.; van Enckevort, W.; Nakamura, T.; Kimura, Y.; Miura, H.; Satoh, H.; Nagashima, K.; Konoto, M. *J. Am. Chem. Soc.* 2011, 133, 8782-8785.

Auto assemblages à 2 éléments: système binaire

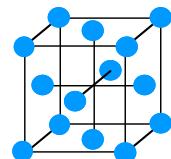


J. V. Sanders, M. J. Murray, ordered arrangements of spheres of two different sizes in opal. *Nature*, 1978, 201-203  
M. J. Murray, J. V. Sanders, Close-packed structures of spheres of two different sizes II. The packing densities of likely arrangements. *Philosophical Magazine A*, 1980, 42, 721-740.

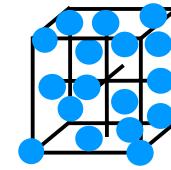
## Matériaux atomiques ordonnés ou non



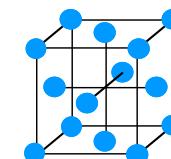
Désordonnés



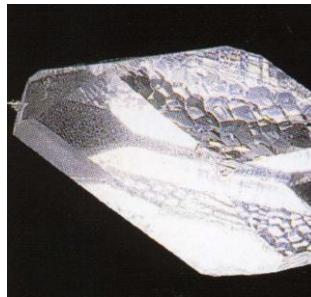
Ordonnés



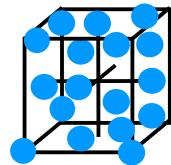
Désordonnés



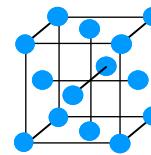
Ordonnés



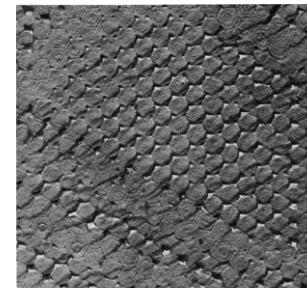
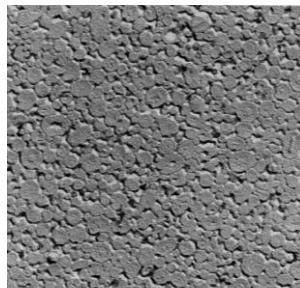
## Microparticules ordonnées ou non



Désordonnées

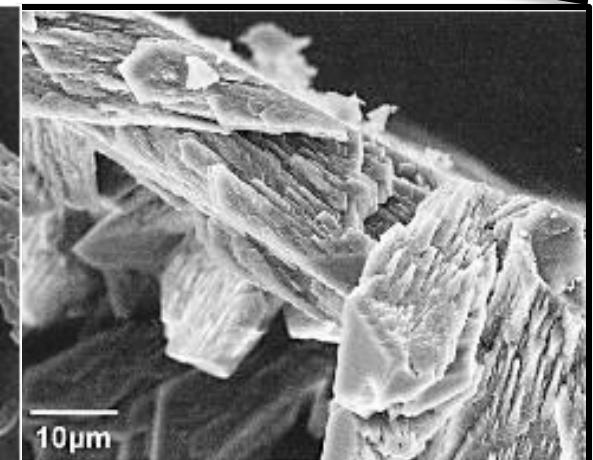
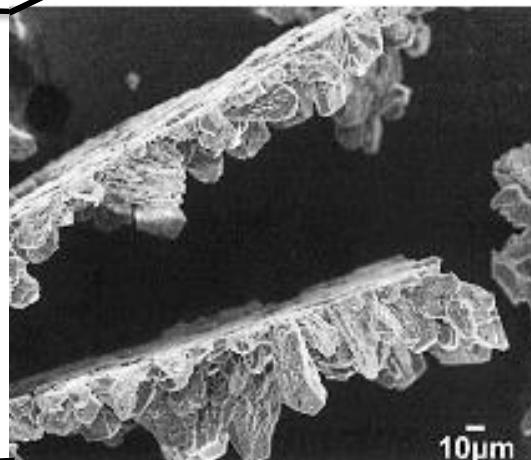
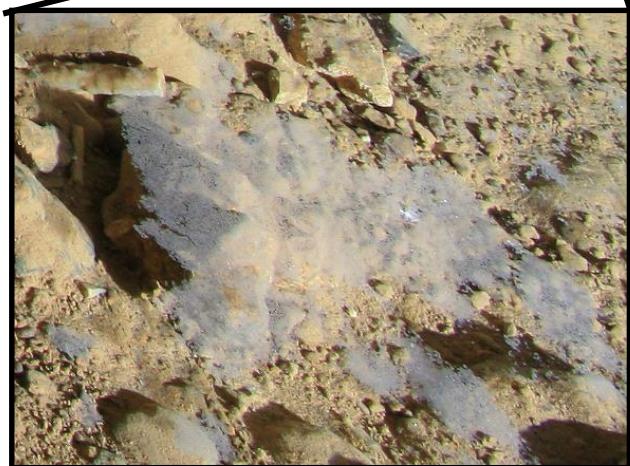


Ordonnées



# Croissance cristalline en milieux confinés

Une grotte au Texas (U.S.A)



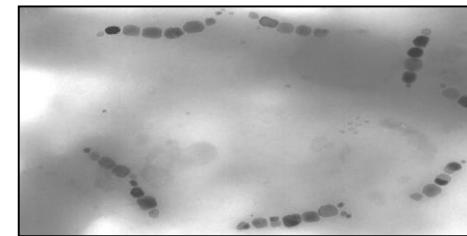
Taylor P. and Chafetz H.S. J. Sed. Res. 2004, 74, 328-341

## Que la Nature nous apprend -t-elle?

Les cristaux atomiques ont une forme spécifique



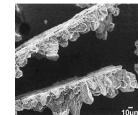
Des microparticules existent dans la Nature et sont susceptibles de s'auto-assembler.



Propriétés spécifiques dues à la cristallinité.



Croissance cristalline à l'interface sous atmosphère saturante



## La matière à différentes échelles

Que la Nature nous apprend-t-elle?

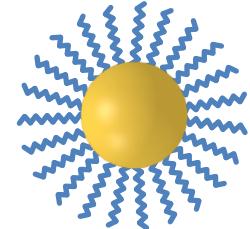
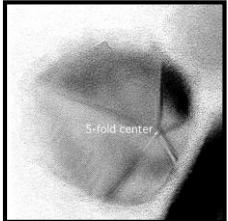
**Nanocristallinité: Cristallinité des nanomatériaux ( ordre des atomes dans une nanoparticule)**

**Supracristaux: assemblage cristallin à 3D de nanocristaux (ordre cristallin des nanocristaux)**

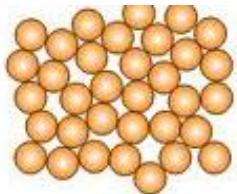
**Propriétés intrinsèques dues à l'autoassemblage cristallin de nanocristaux.**

**Analogies entre les supracristaux et les cristaux atomiques.**

## Nanocristallinité: Structure cristalline de nanoparticules.



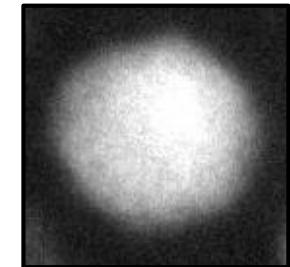
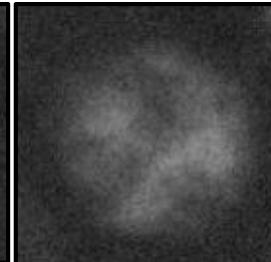
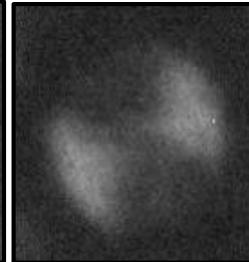
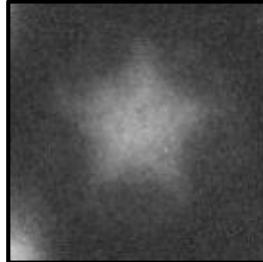
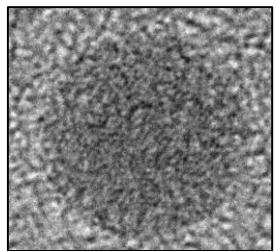
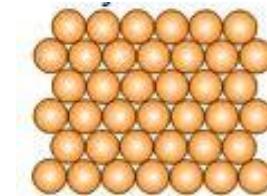
Amorphe



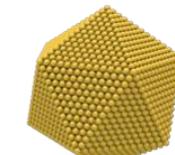
defauts



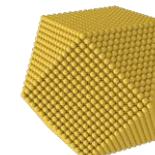
mono cristal



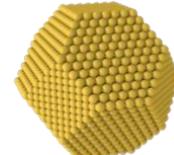
decahedre



icosahedre



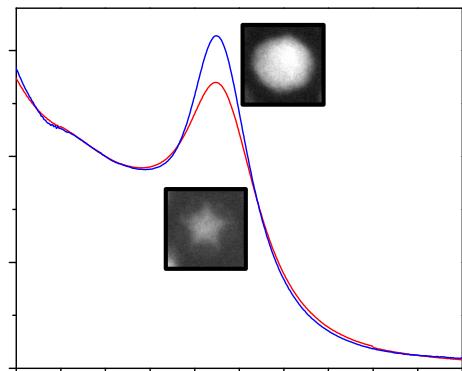
cuboctahedre



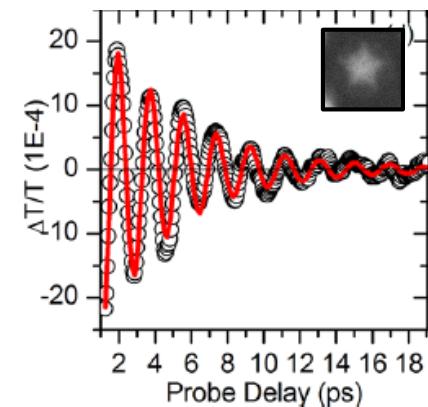
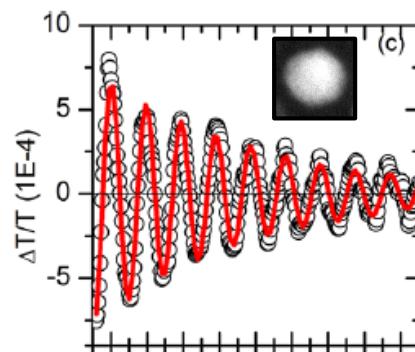
Octahedre  
tronqué

# Propriétés Physiques

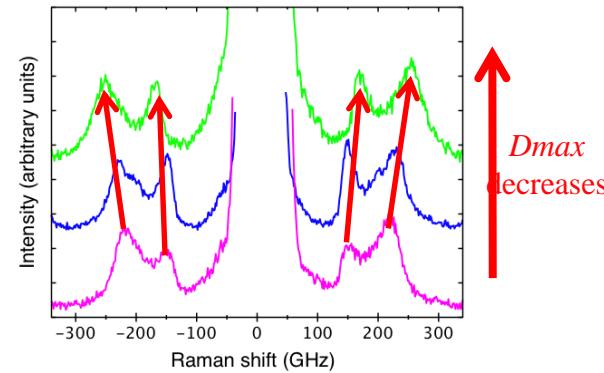
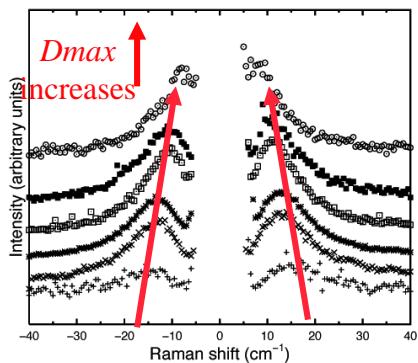
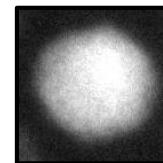
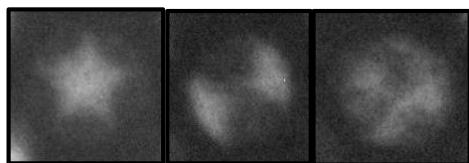
## Absorption



## Mode de respiration ( $I=0$ )

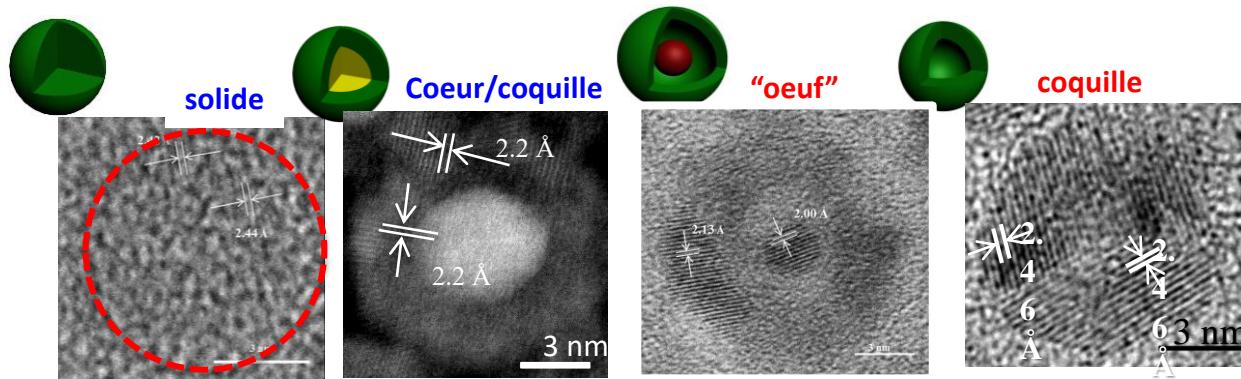


## Mode quadrupolaire ( $I=2$ ): Raman basse fréquence

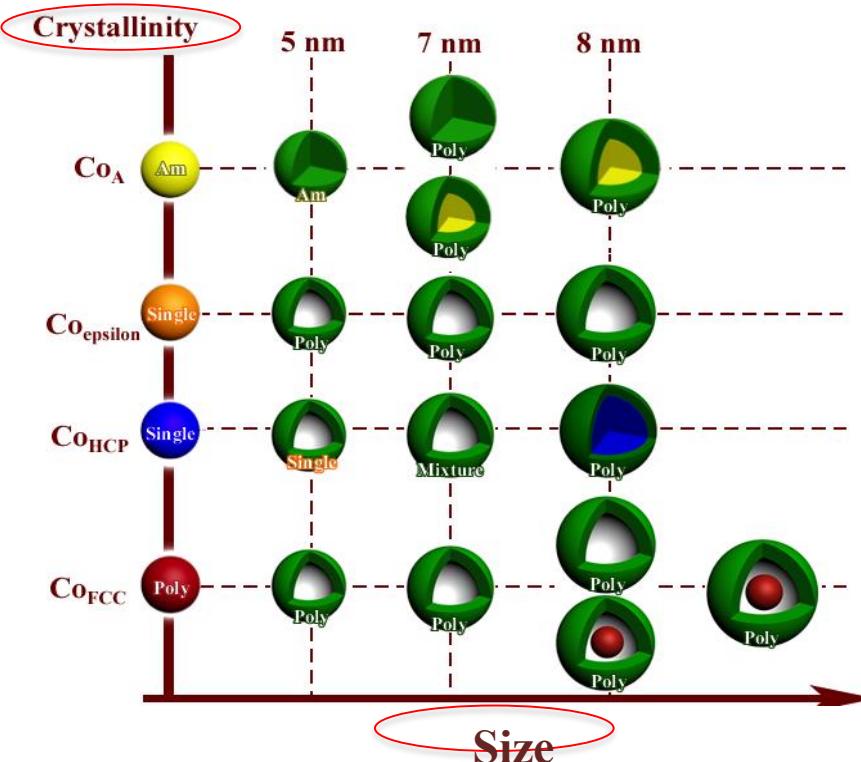
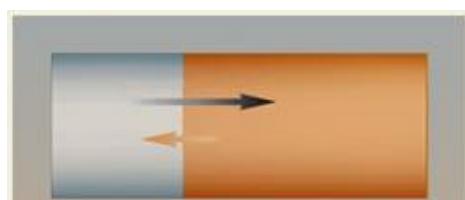


H. Portales, N. Goubet, L. Saviot, S. Adichtchev, D.B. Murray, A. Mermet, E. Duval and M.P. Pileni Proc. Natl. Acad. Sci. USA 105, 14784 (2008) H. Portales, N. Goubet, L. Saviot, P. Yang, S. Sirotnik, E. Duval, A. Mermet, M.P. Pileni, ACS Nano 4, 3490-3497

## Propriétés chimiques intrinsèques dues à la nanocrystallinité de nanocristaux de cobalt.



### Effet Kirkendall



## Nanocristallinité: Cristallinité des nanomatériaux ( ordre des atomes dans une nanoparticule)

- \* Quelques propriétés spécifiques dues à la nanocristallinité.
- \* La structure finale due à l'oxidation des nanocristaux de cobalt évolue selon la nanocristallinité.

## La matière à différentes échelles

Que la Nature nous apprend-t-elle?

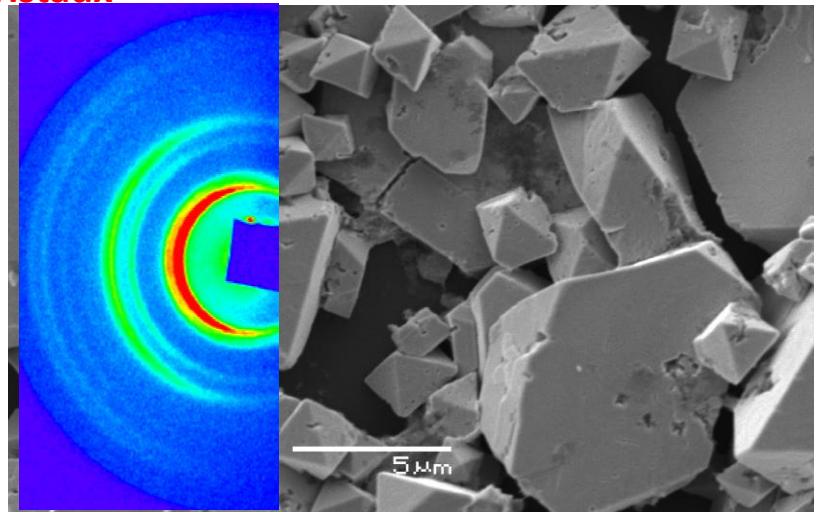
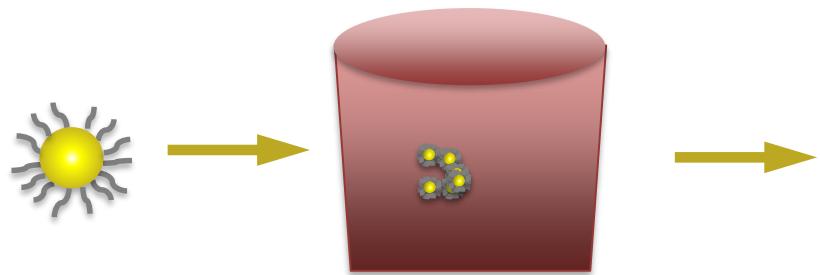
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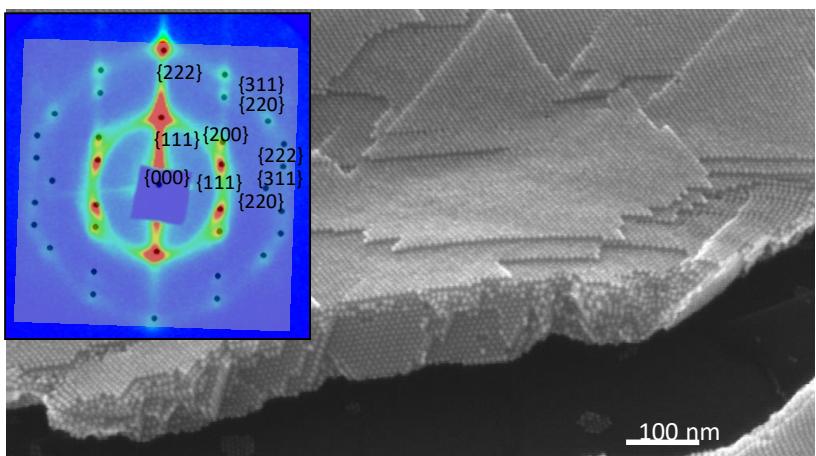
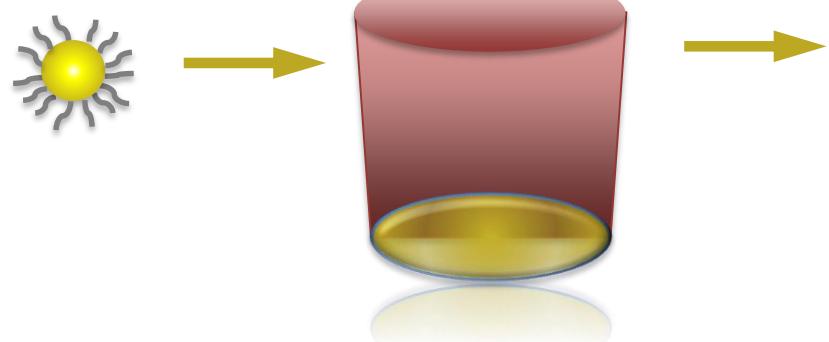
**Propriétés intrinsèques dues à l'autoassemblage cristallin de nanocristaux.**

**Analogies entre les supracristaux et les cristaux atomiques.**

## Processus de croissance cristalline de supracristaux



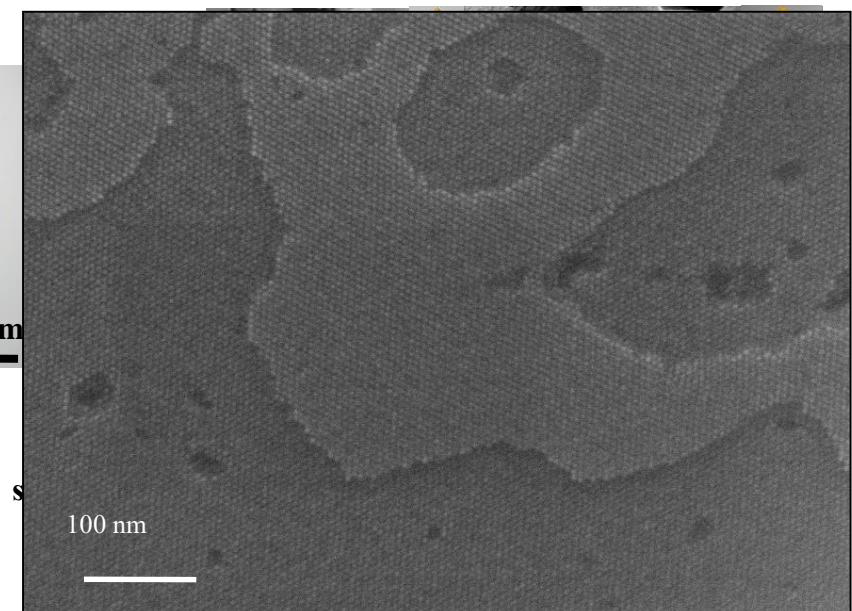
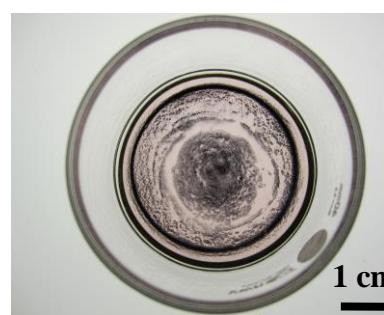
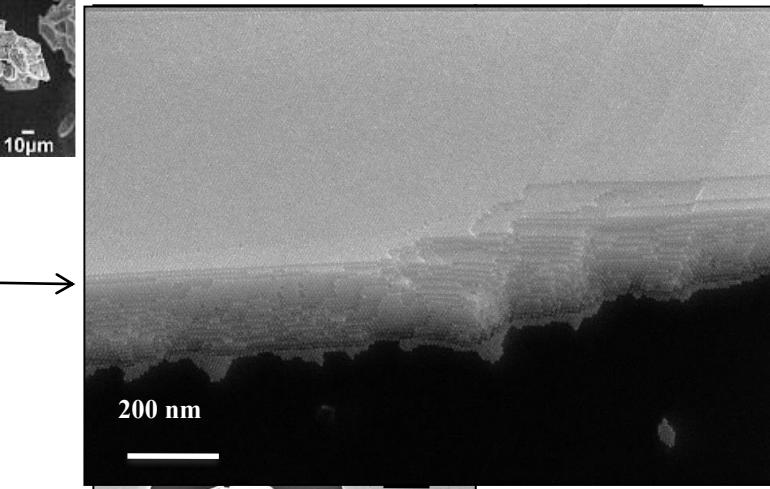
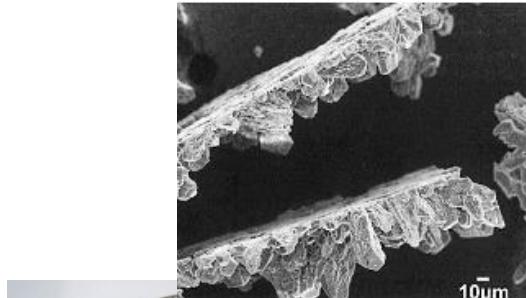
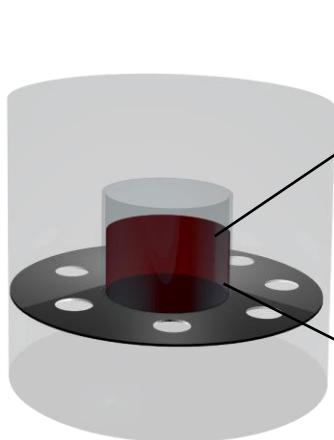
Croissance homogène



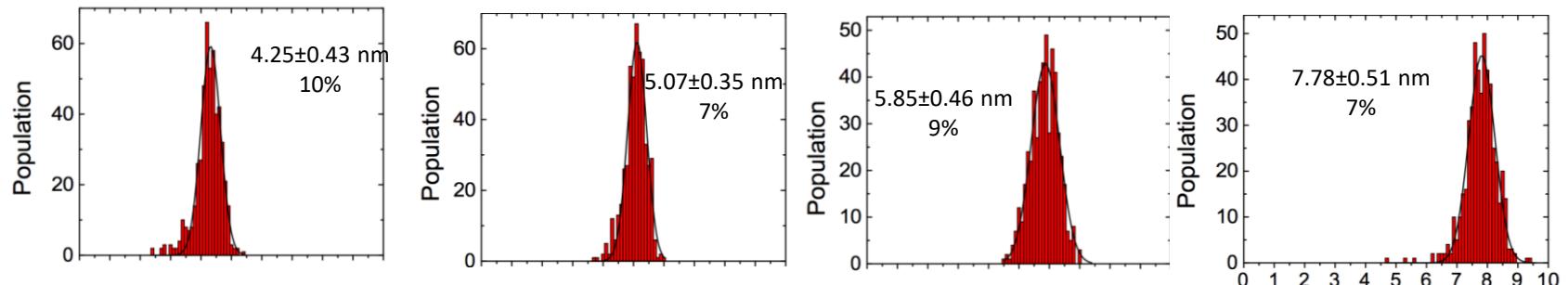
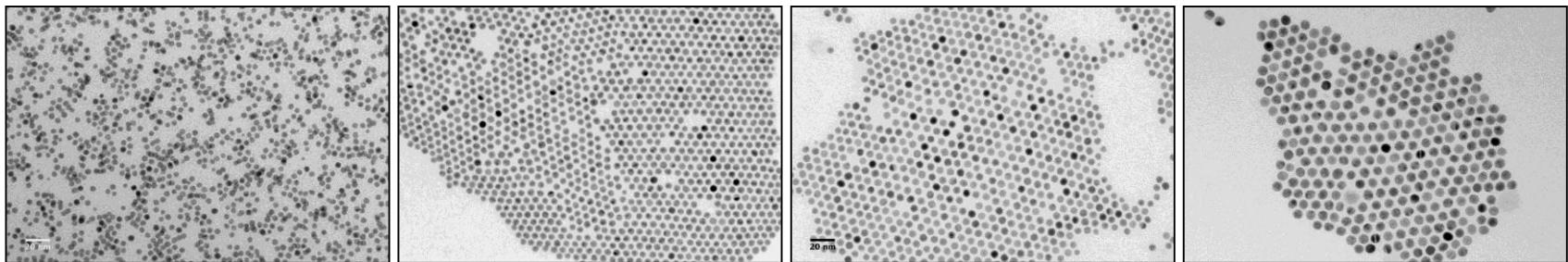
Croissance hétérogène

L. Motte, F. Billoudet and M.P. Pileni J. Phys. Chem.; 99, 16425-16429, (1995) A. Courty, C. Fermon, and M.P. Pileni Adv. Mater. 13, 254-258 (2001), N.Goubet., H. Portalès., C.Yang., I. Arfaoui, P.A. Albouy , A. Mermet. And M.P. Pileni J. Am. Chem.Soc., 134, 3714-3719, (2012). N.Goubet, J.Richardi, P.A. Albouy and M.P.Pileni J.Phys.Chem.B., 117, 4510, (2013). YF. Wan, N. Goubet, P. A. Albouy and M. P. Pileni. Langmuir 29, 7456, (2013). Y.F.Wan, N.Goubet, P.A. Albouy and M.P.Pileni Langmuir 29, 13576, (2013). N. Schaeffer, Y.Wan, M.P. Pileni. Langmuir , 30, 7177 (2014)

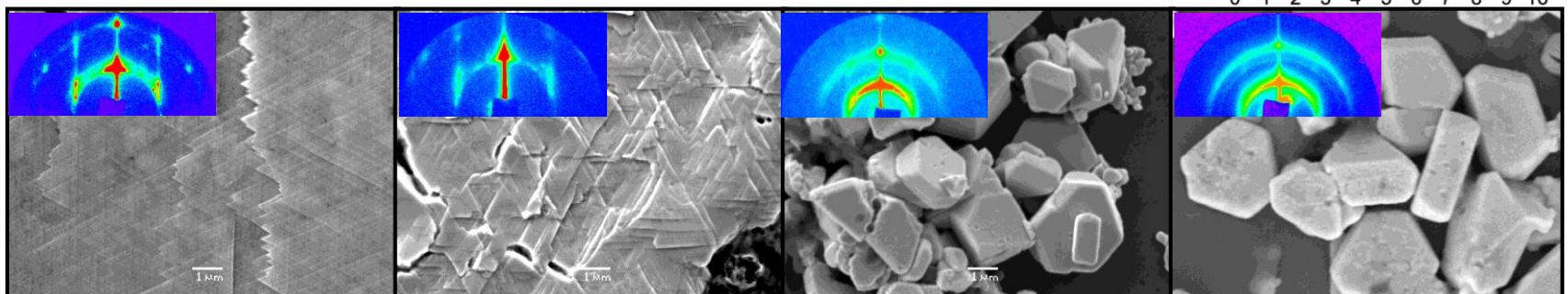
## Croissance cristalline en milieux confinés



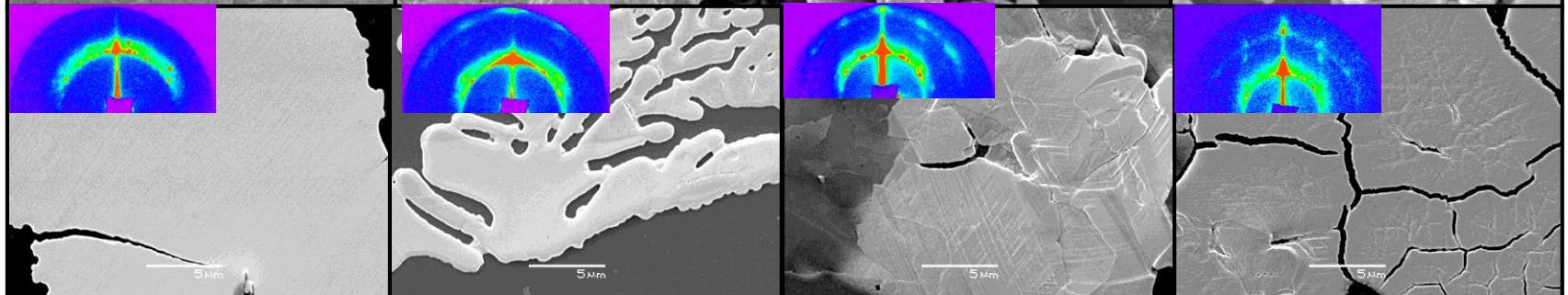
# Croissance cristalline de nanocristaux d'or



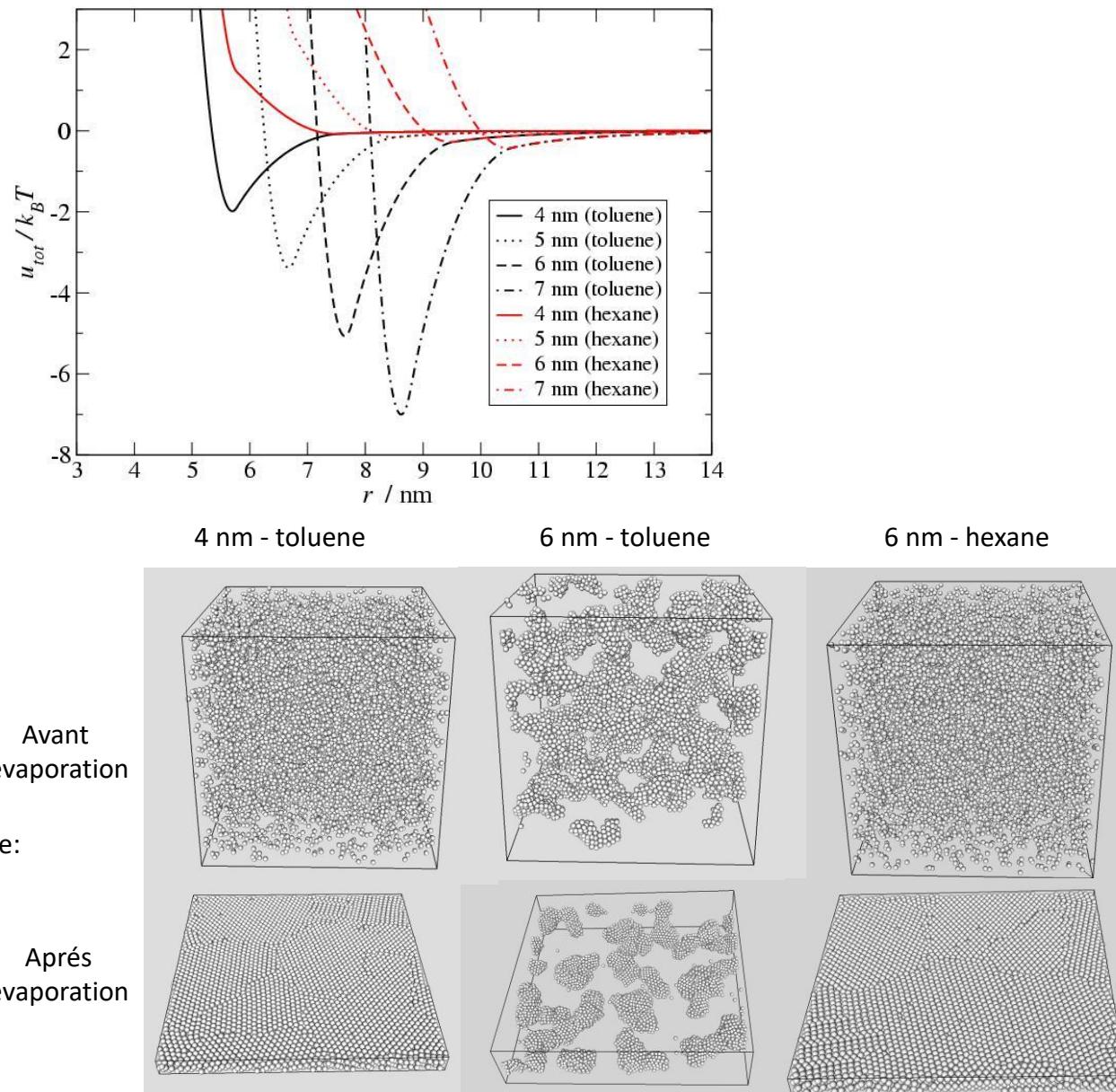
Toluène



Hexane



# Prédiction de croissance de supracristaux

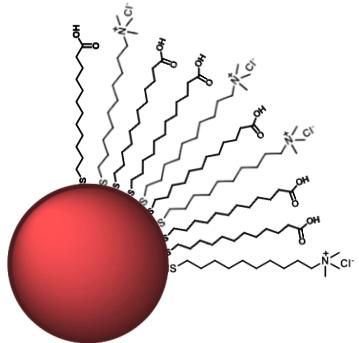


## Simulation dynamique

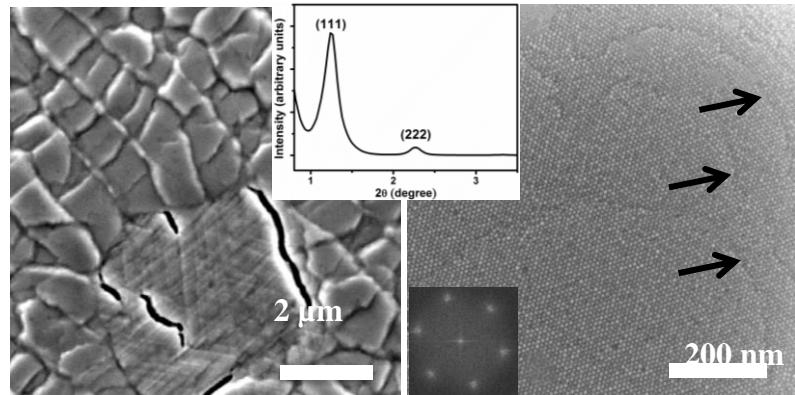
influence du l'évaporation sur la structure finale:

- substrate: mur au fond de la boîte
- haut de la boîte: liquide-gaz interface

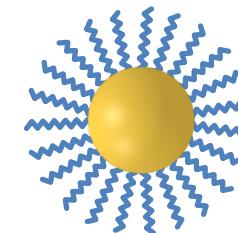
# Transition d'un processus de croissance homogène vers un processus hétérogène.



Nanocristaux soluble dans l'eau

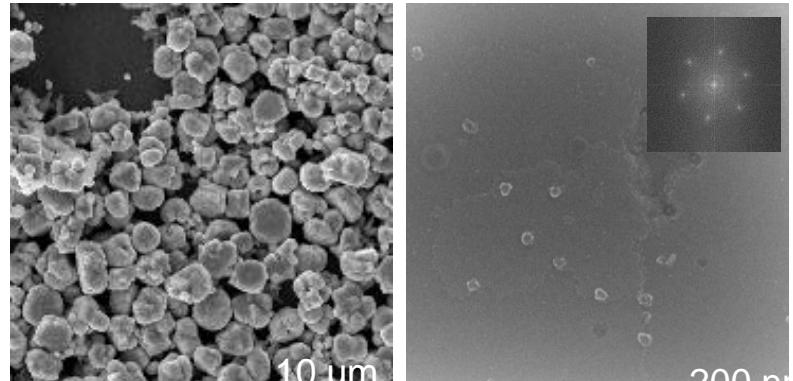
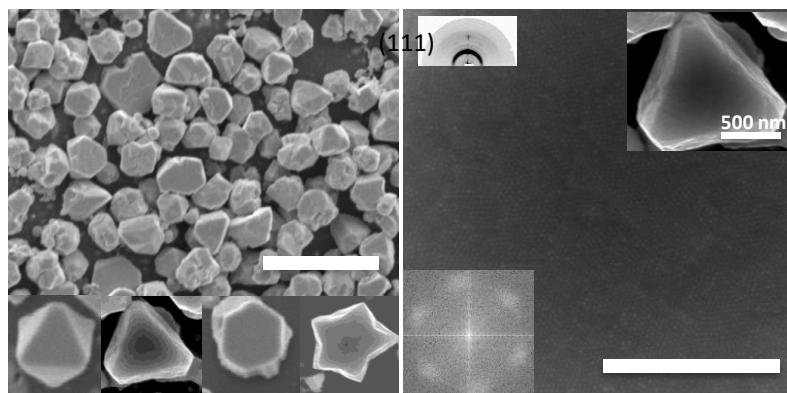
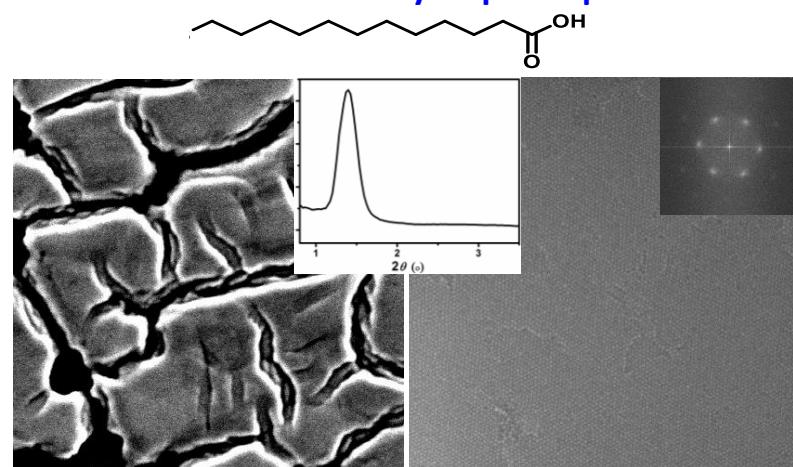


Nanocristaux dispersés dans  
un "bon" solvant pour les  
chaines

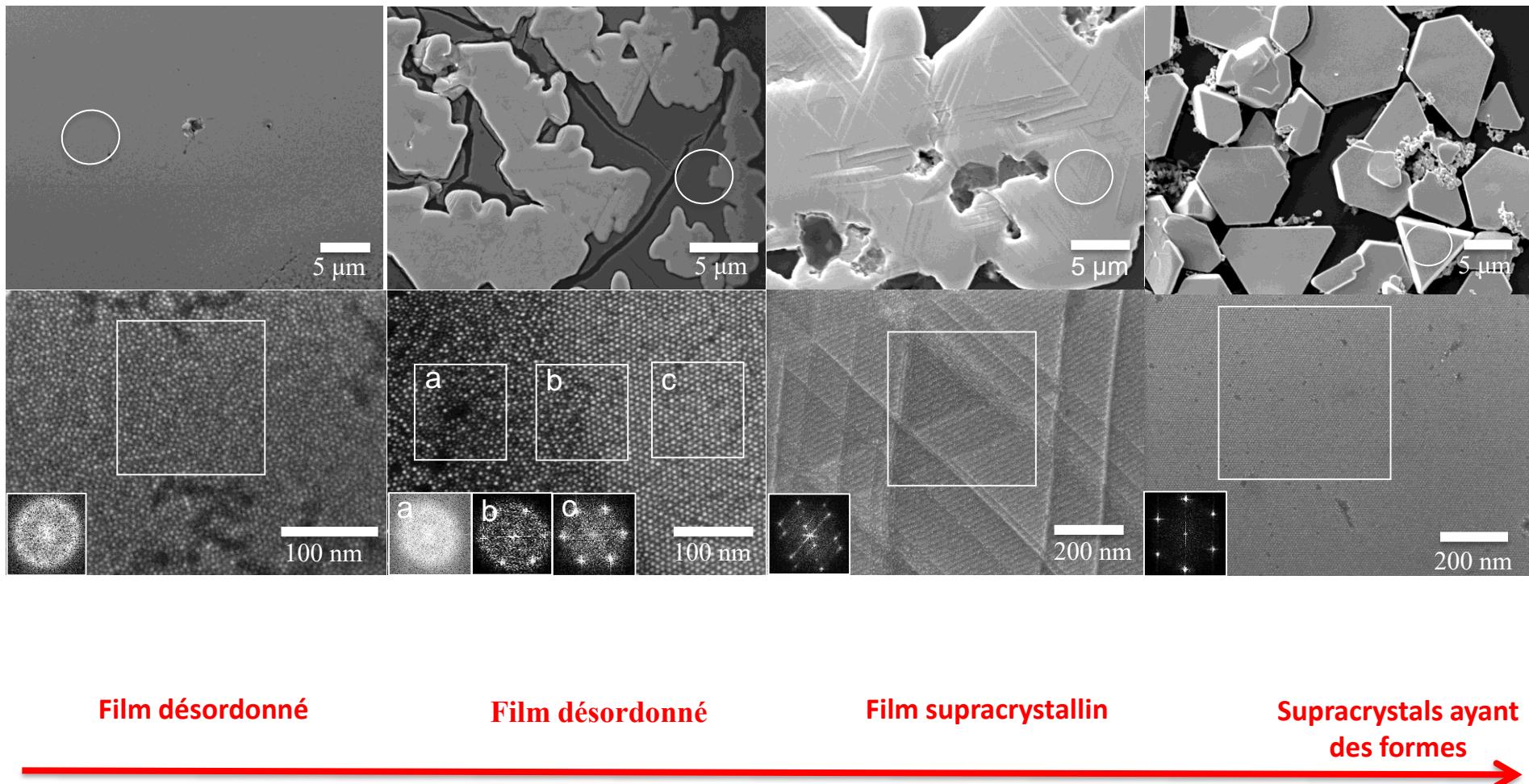


un "mauvais" solvant pour les chaines

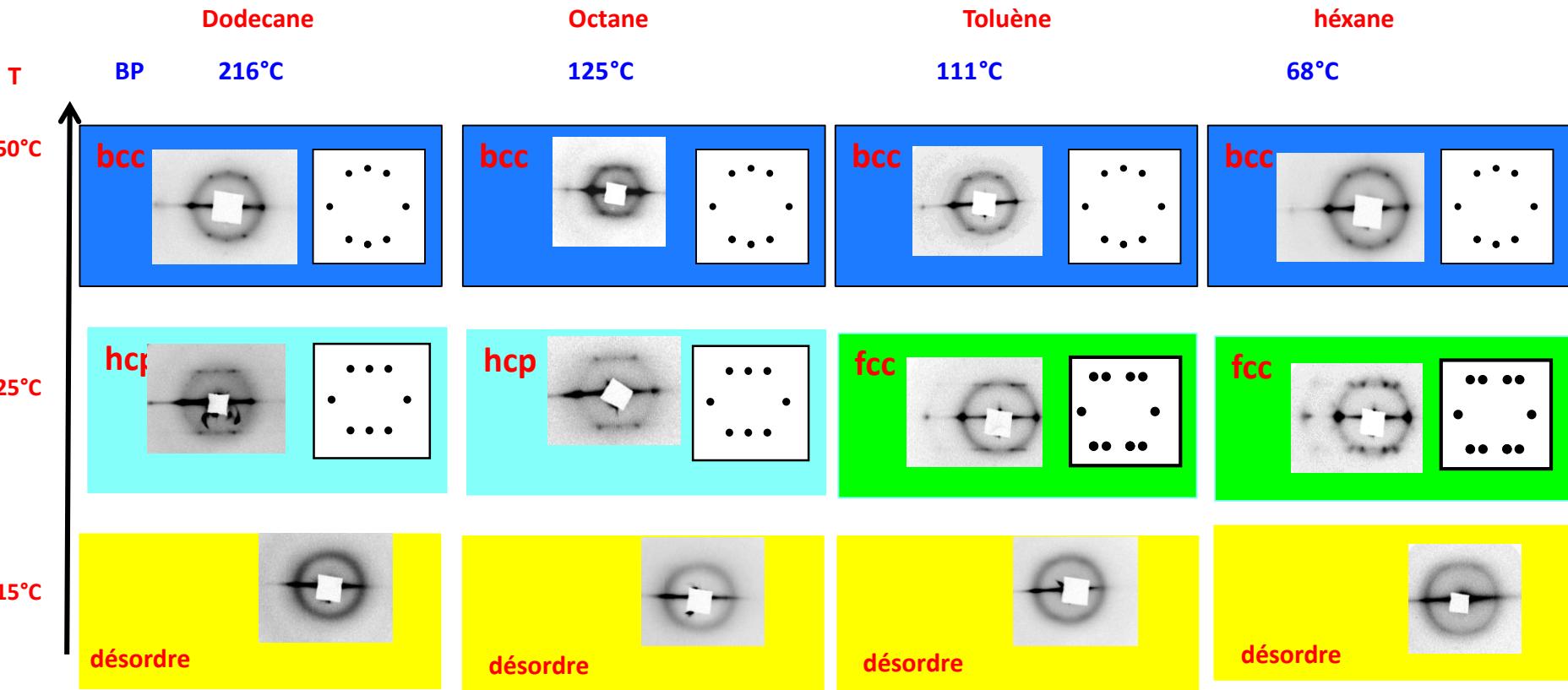
Nanocristaux hydrophobiques



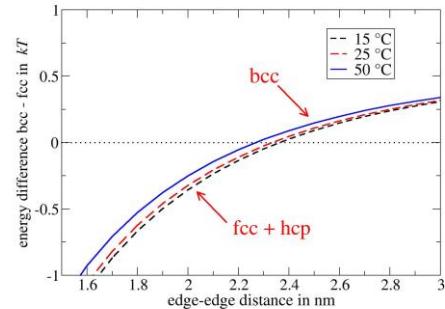
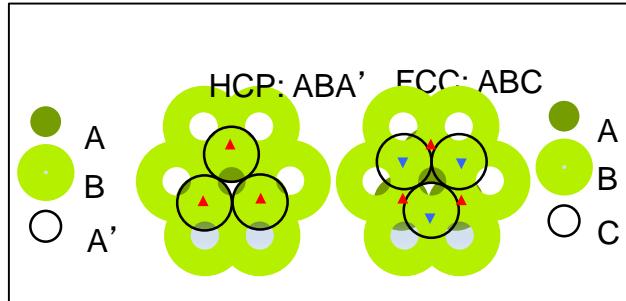
## Hierarchie dans la croissance cristalline des supracristaux



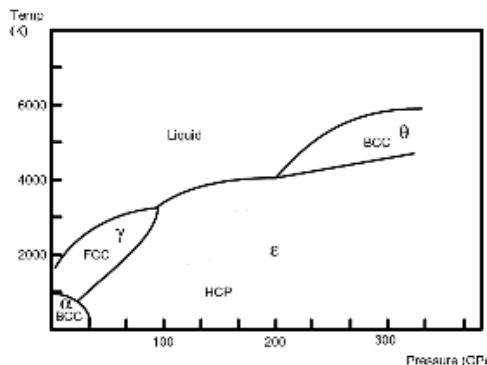
# Diagramme de phase de supracrystals



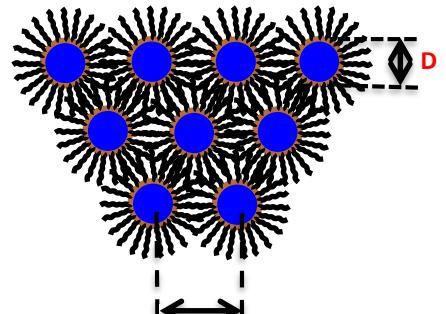
▲ Tetrahedral interstice between A and B  
▼ Tetrahedral interstice between B and C



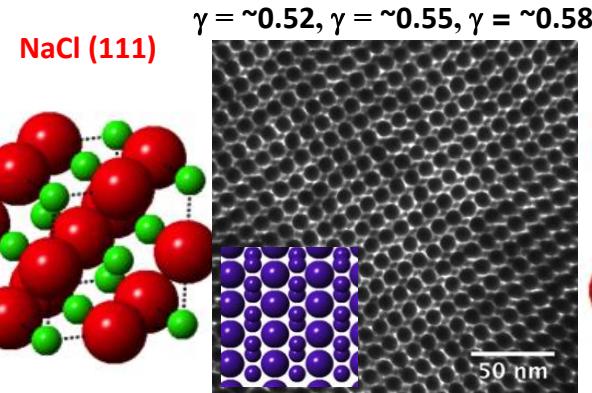
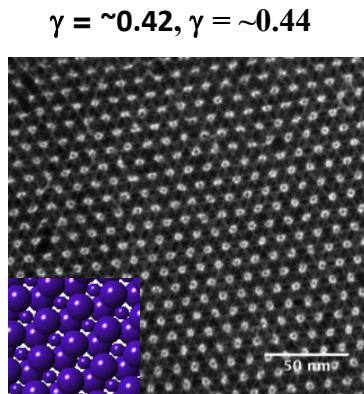
# Diagramme de phase du Fe



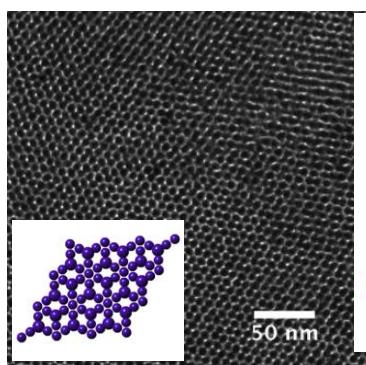
# Auto assemblages de deux types de nanocristaux



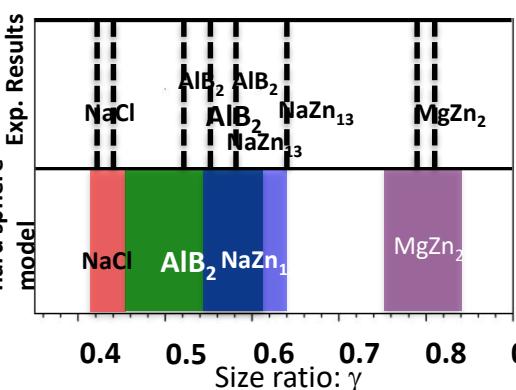
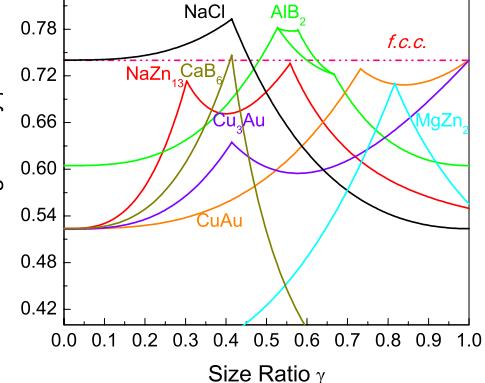
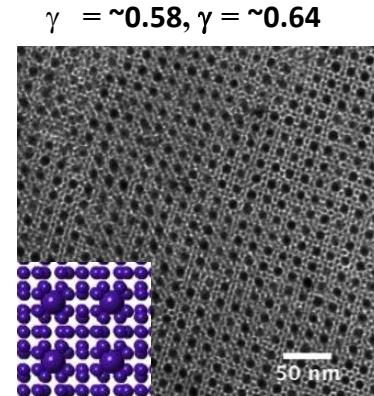
\* Effective size ratio  $\gamma = (D_{\text{eff}})_s / (D_{\text{eff}})_L$



$\gamma = \sim 0.79, \gamma = \sim 0.81$

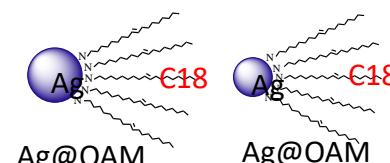


$\gamma = \sim 0.58, \gamma = \sim 0.64$



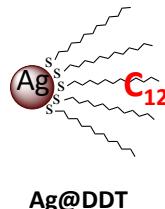
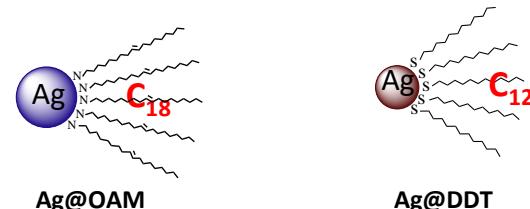
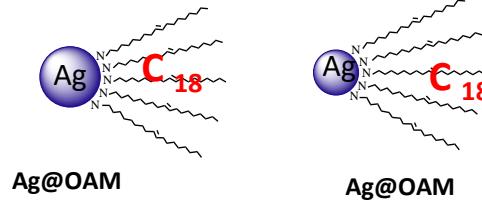
NaCl      AlB<sub>2</sub>      NaZn<sub>13</sub>      MgZn<sub>2</sub>

NaCl      AlB<sub>2</sub>      NaZn<sub>13</sub>

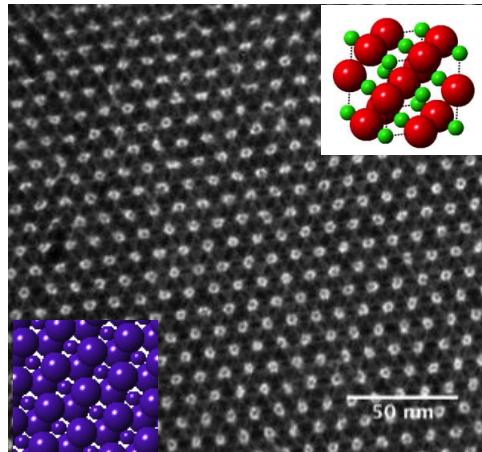


# Auto assemblages de deux types de nanocristaux

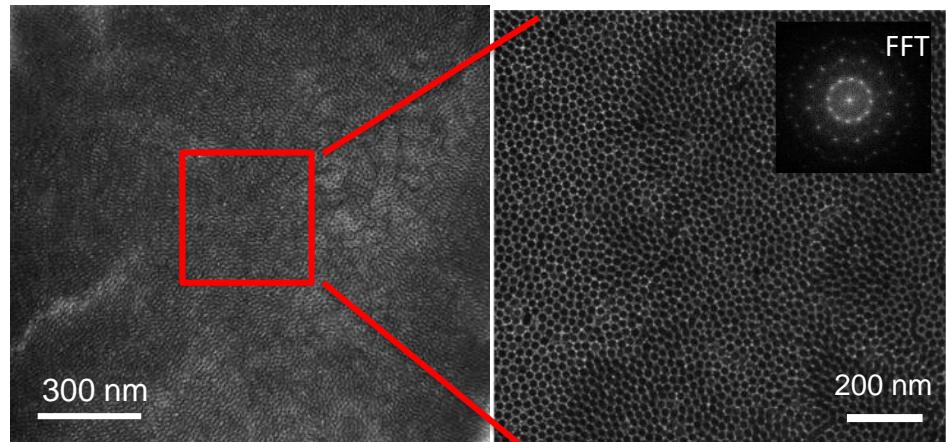
$$\gamma = \sim 0.42$$



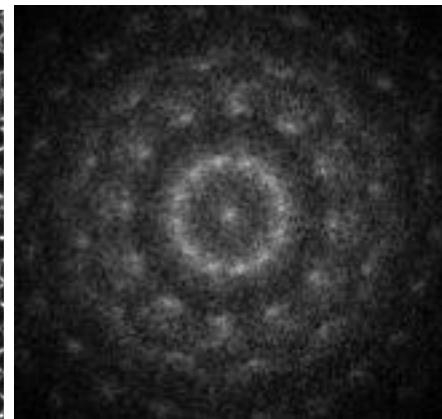
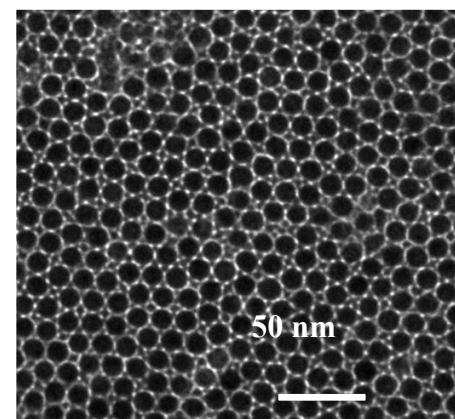
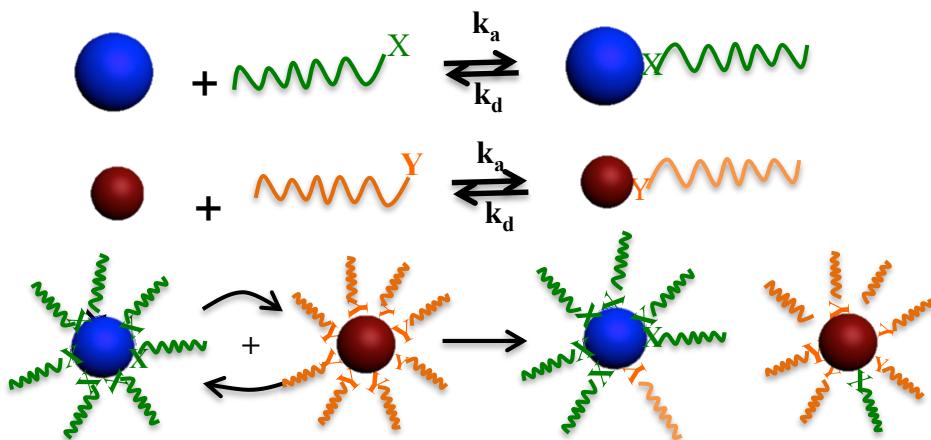
NaCl (111)



Quasicrystal



Dodecagonal “quasi” supra crystal



## **\*Nanocristallinité l'échelle mésoscopique: supracristaux et propriétés**

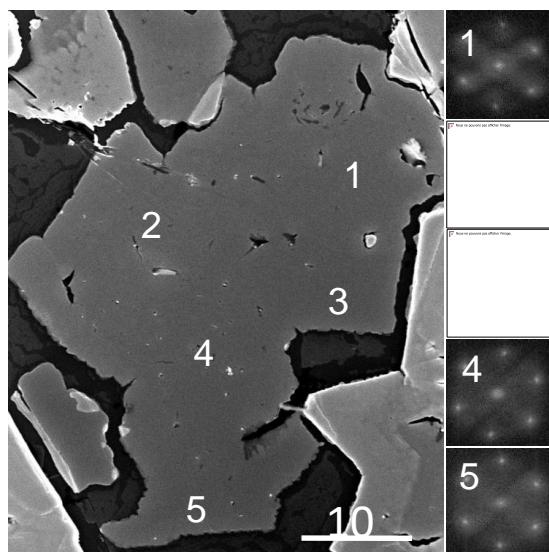
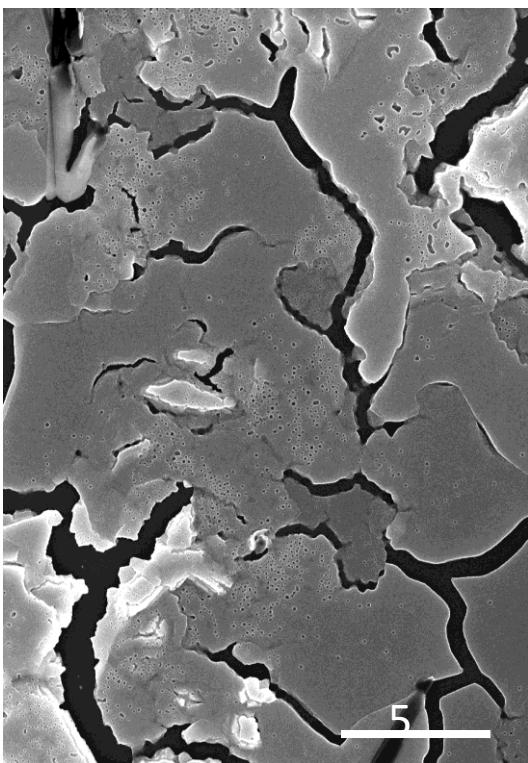
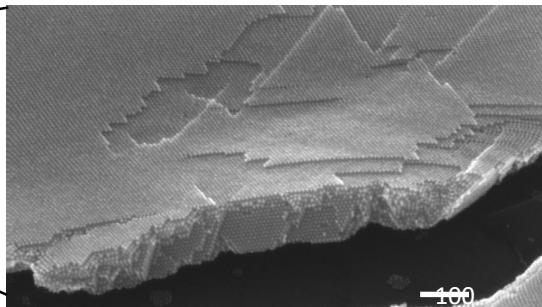
Ségrégation de nanocristaux

Surfaces vicinale

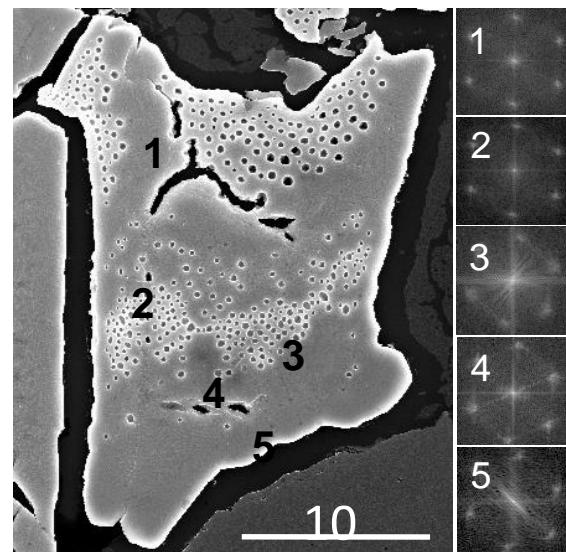
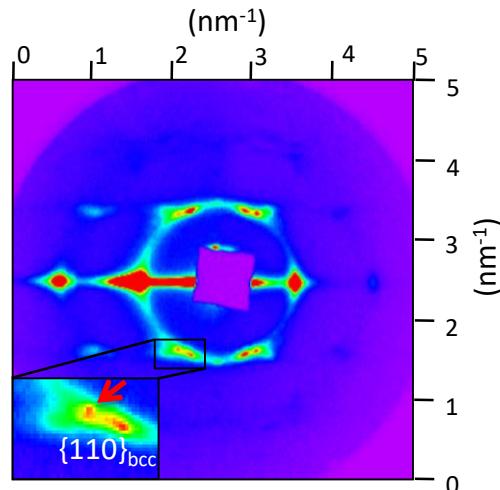
Négatif supracristaux

Quasi supracristaux

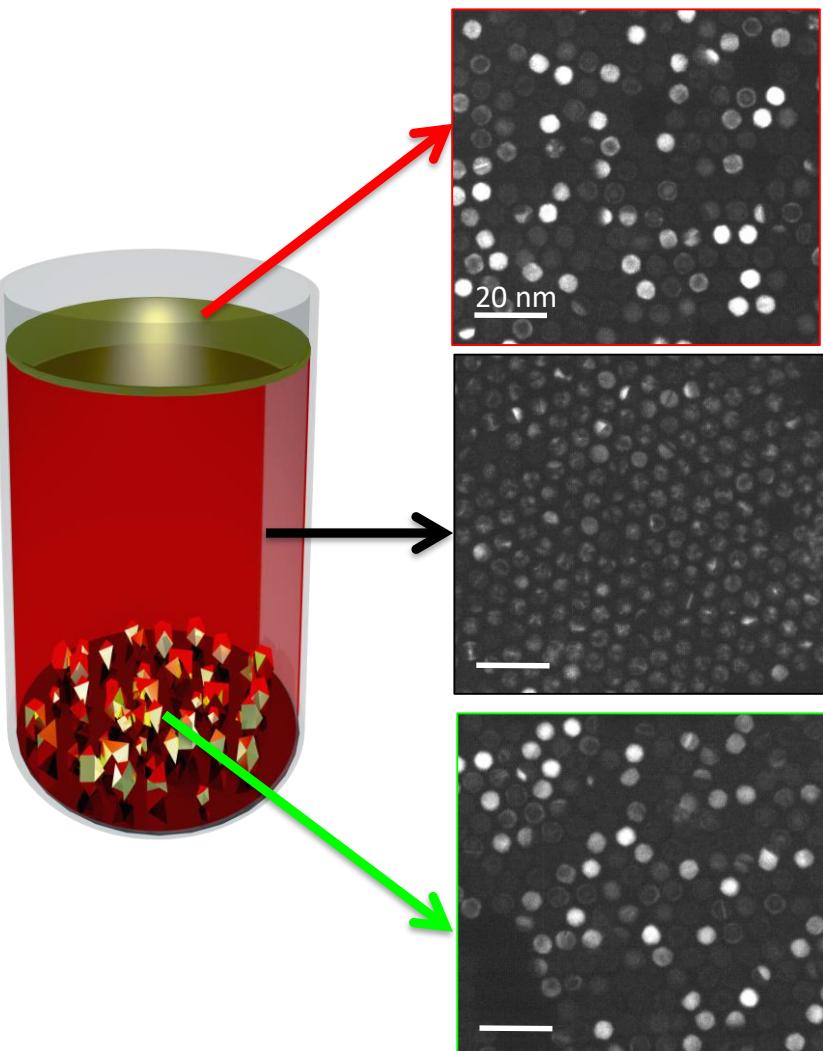
## Film fin de supracristaux



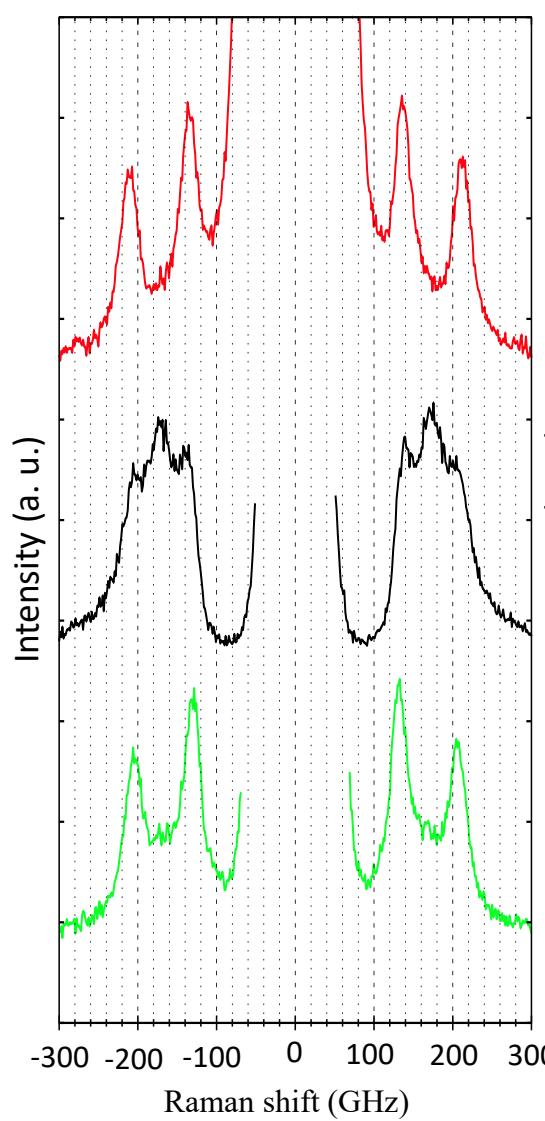
Mixture of FCC and BCC supracrystals



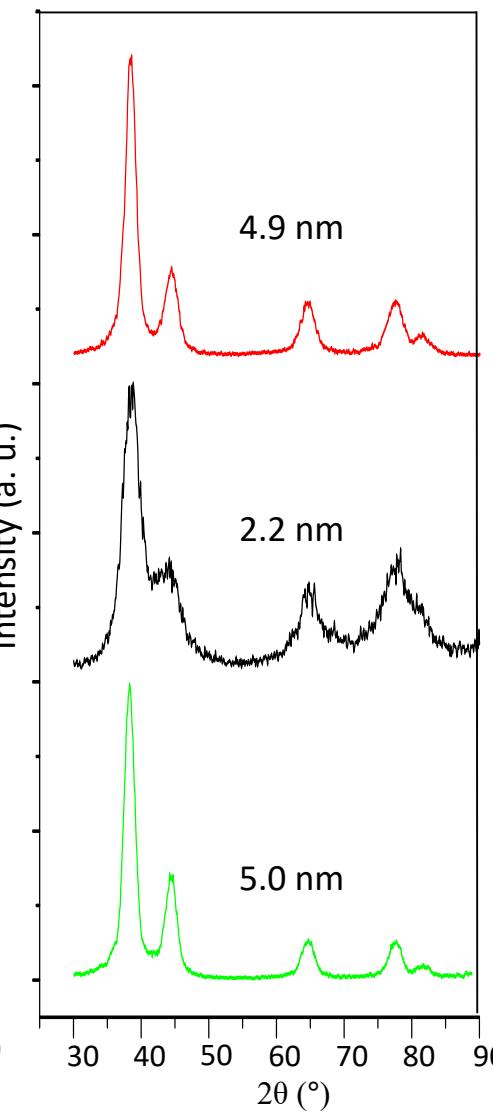
# Nanocrystallinity Selection



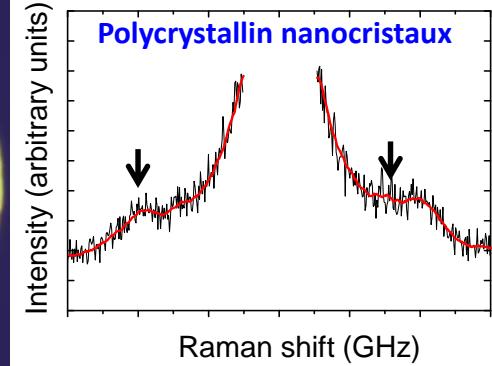
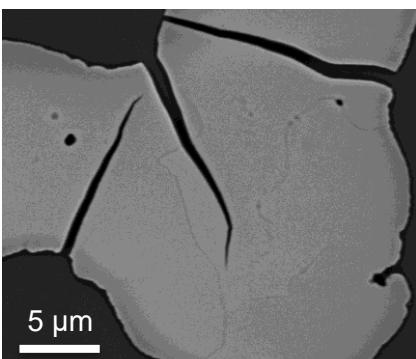
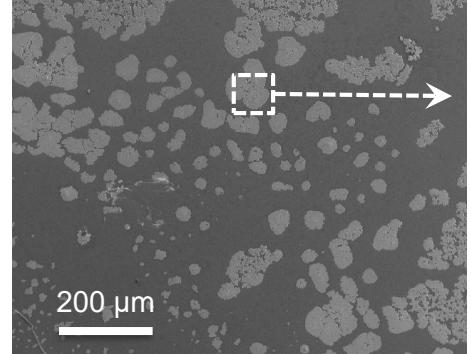
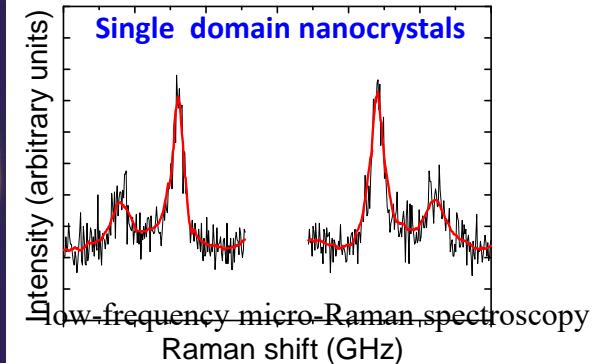
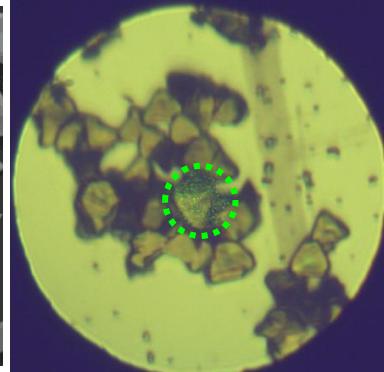
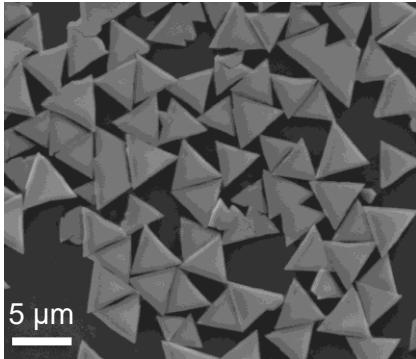
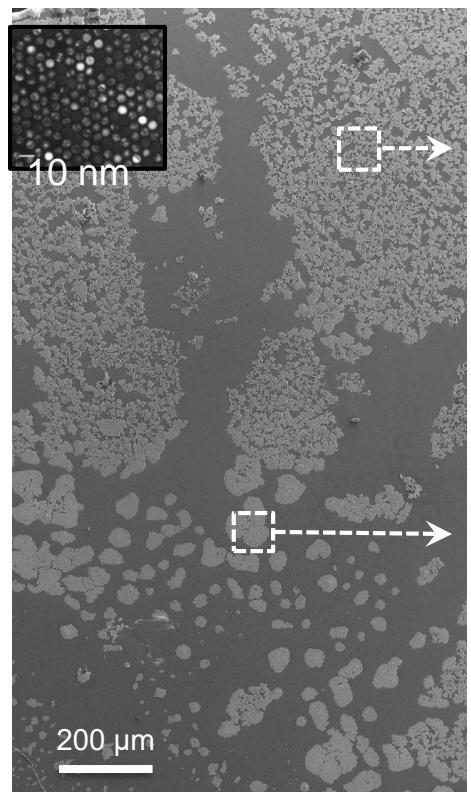
Raman basse fréquence



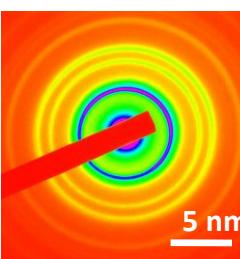
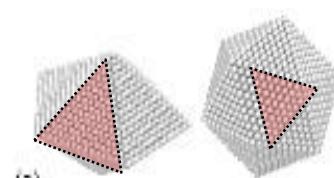
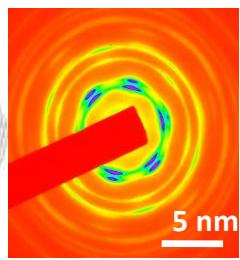
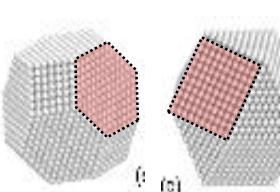
Diffraction



# Ségrégation de nanocristaux

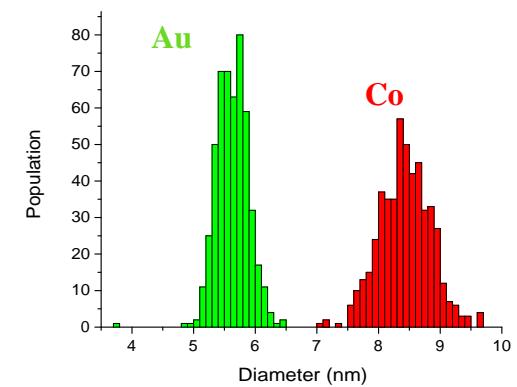
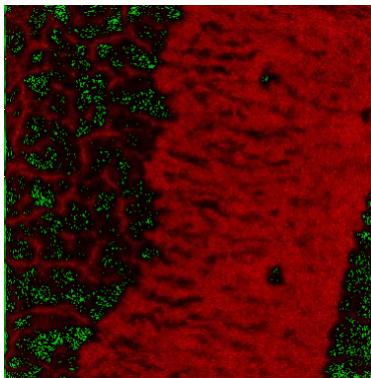
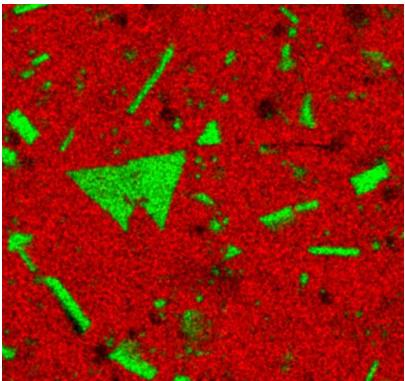


## Mono cristaux

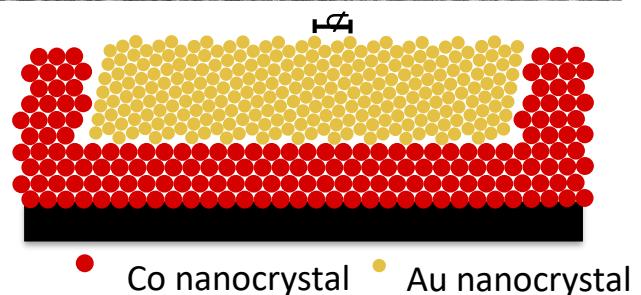
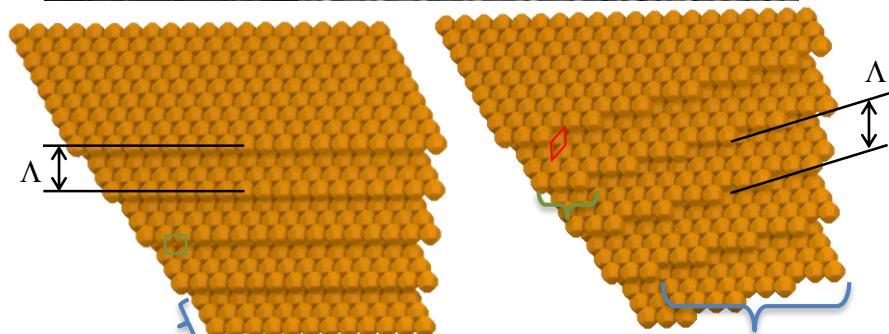
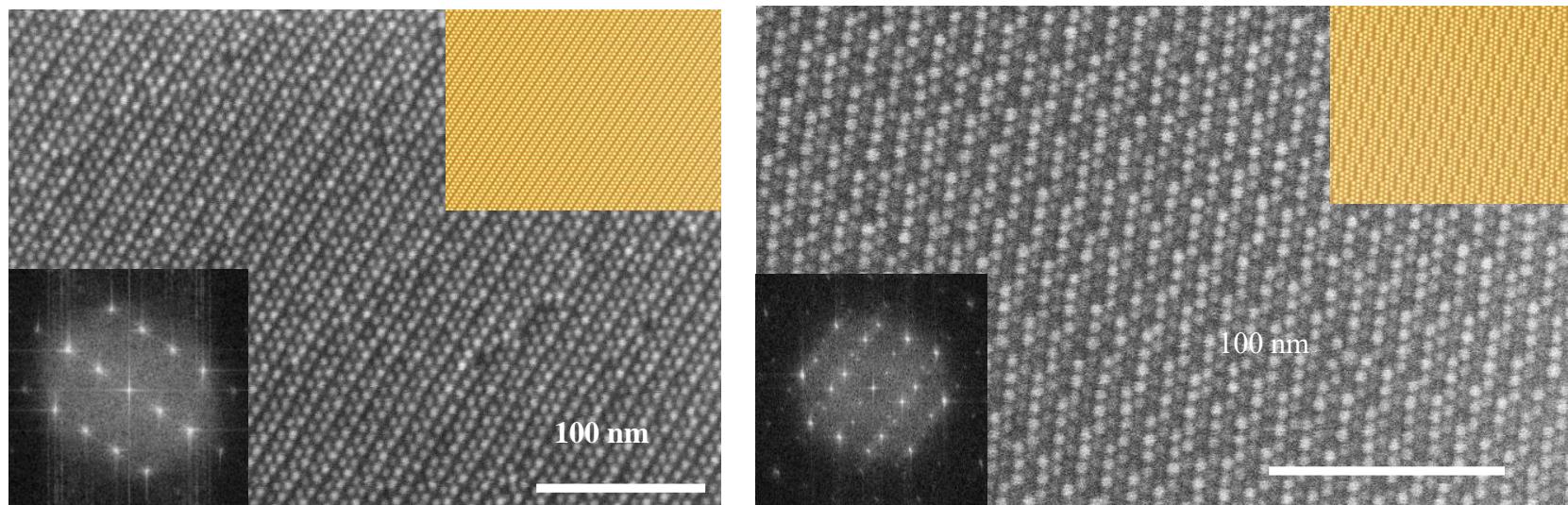


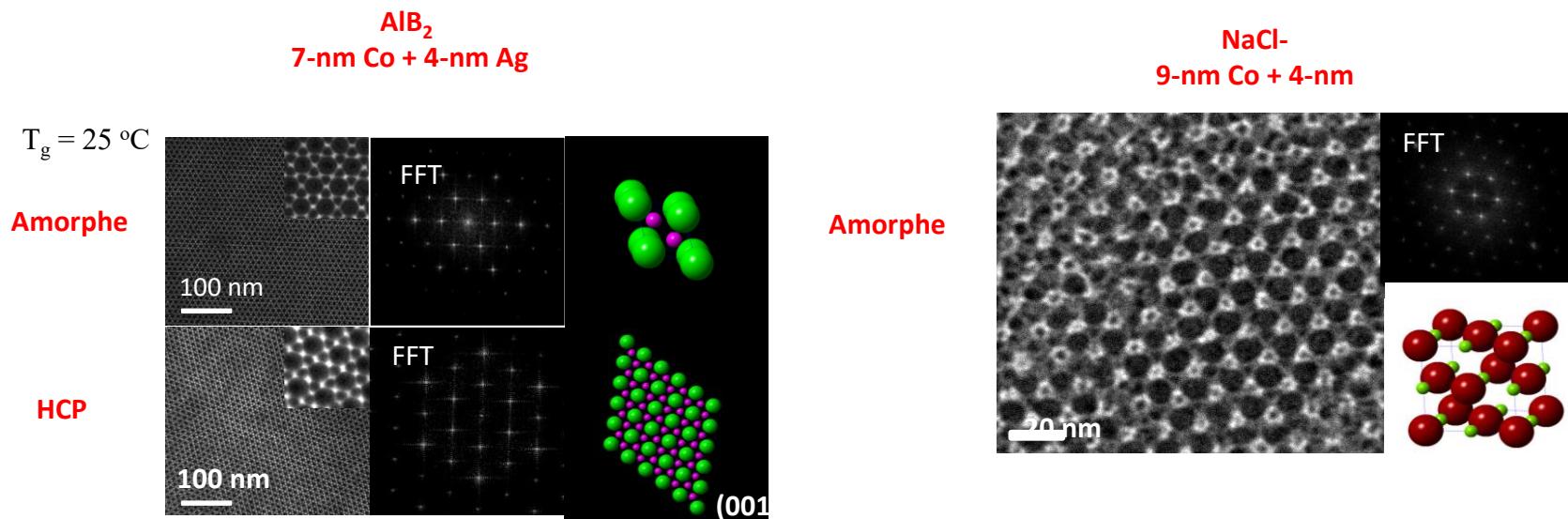
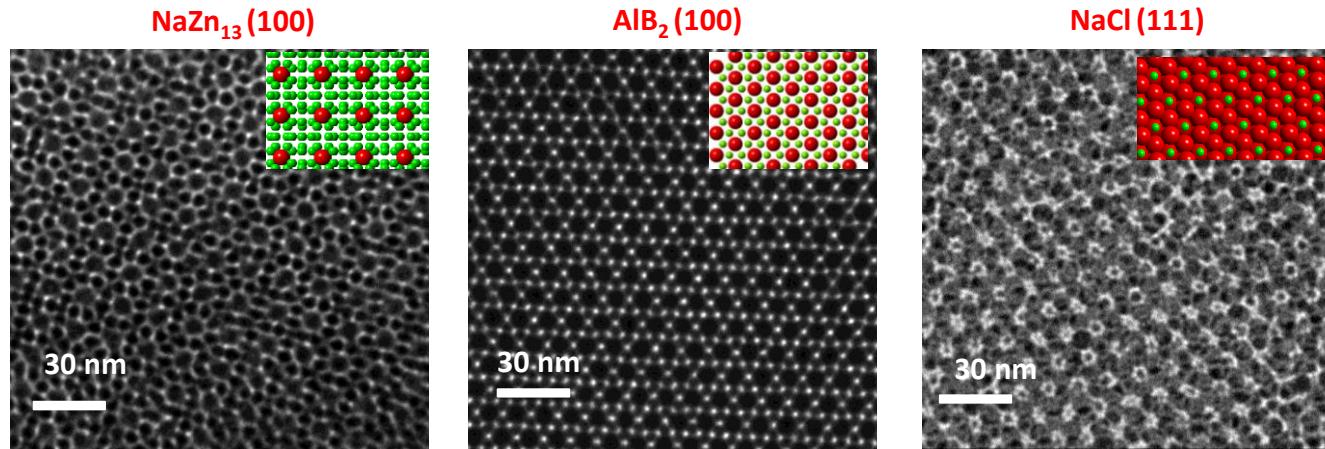
## Polycristaux

## Nanocrystallinité: surfaces vicinales



Growth on a underlying Co nanocrystal film





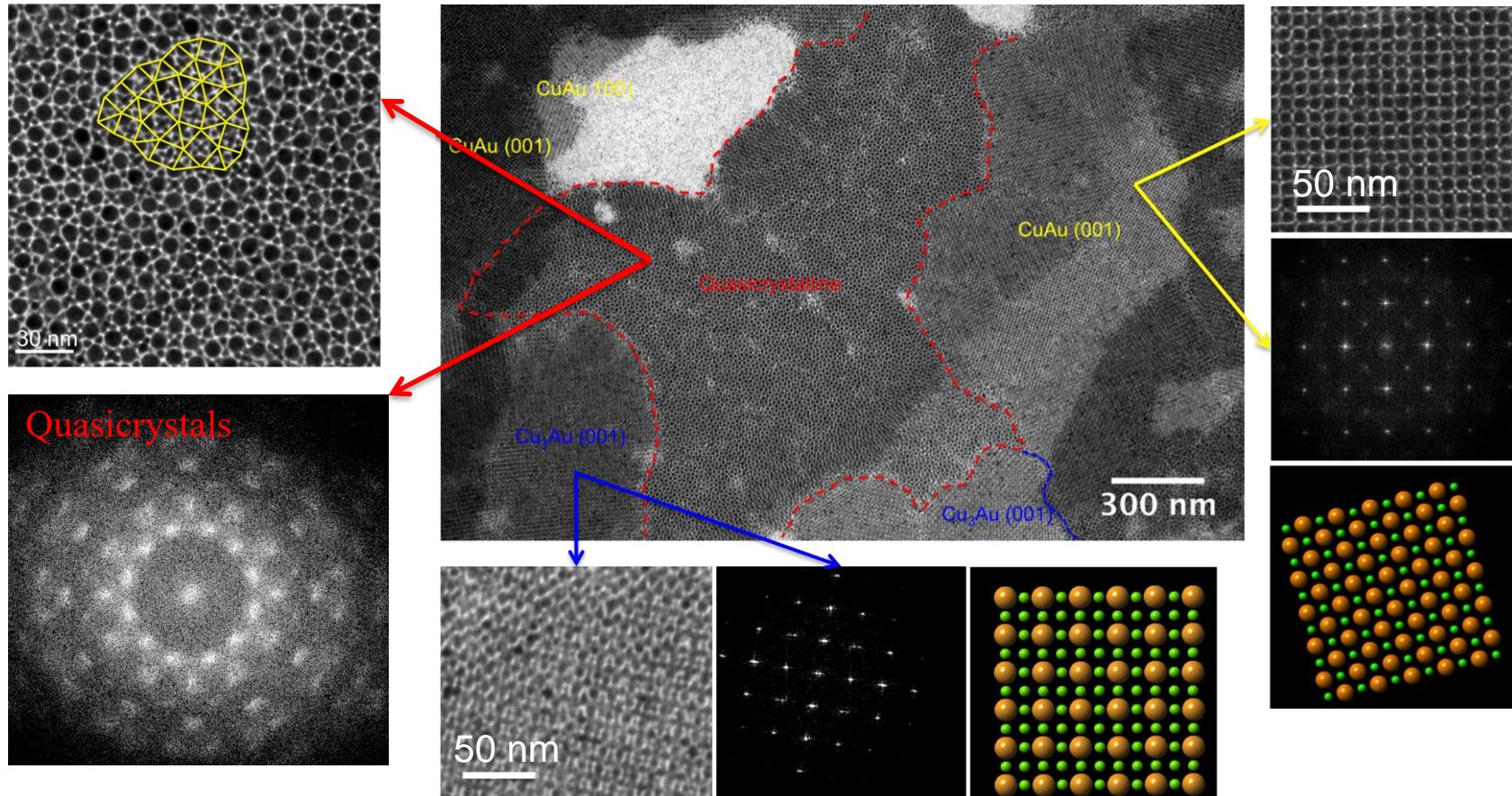
Binary systems: Co/Ag: Ferromagnetic hcp  
Co single domain nanocrystals

9-nm Co + 4-nm Ag

$T_g = 25^\circ\text{C}$

$[\text{Co}]/[\text{Ag}] = \frac{1}{2}$

Co: hpc

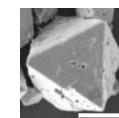
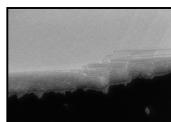


Différentes structures: CoAg, CoAg<sub>3</sub> et quasicristal ordre

\* Deux types de croissance cristalline

Homeogène

Hétérogène



\* Transition de processus de croissance: hétérogène / homogène

\* Hierarchie dans les processus de croissance des supracristaux

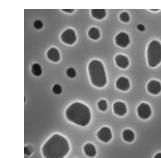
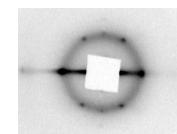
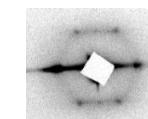
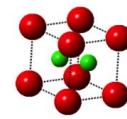
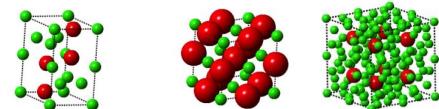
\* Diagramme de phase semblable à celle des cristaux atomiques

\* Processus de ségrégation de nanocristaux

\* supracristaux négatifs

\* Système binaire

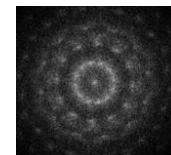
\* Echange de ligands



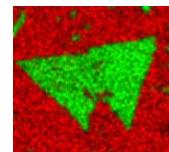
\* Quasi supracristaux induit par

Echange des ligands

Interactions magnétiques



\* Surface vicinale



## La matière à différentes échelles

Que la Nature nous apprend-t-elle?

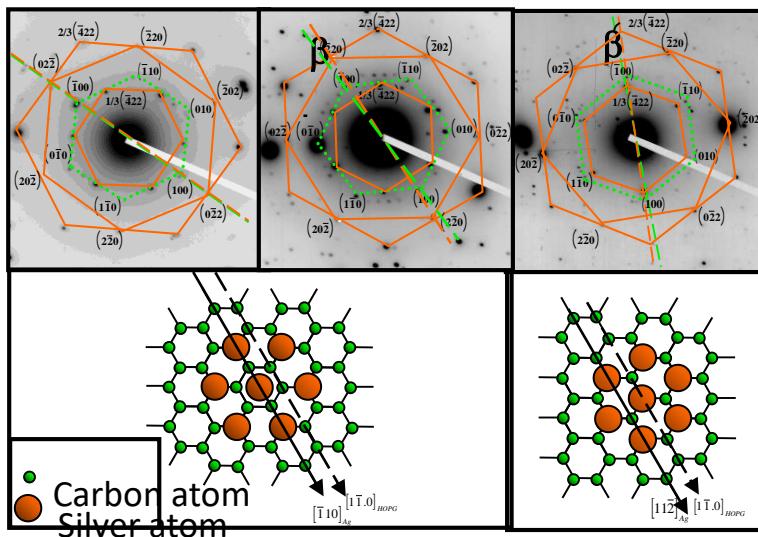
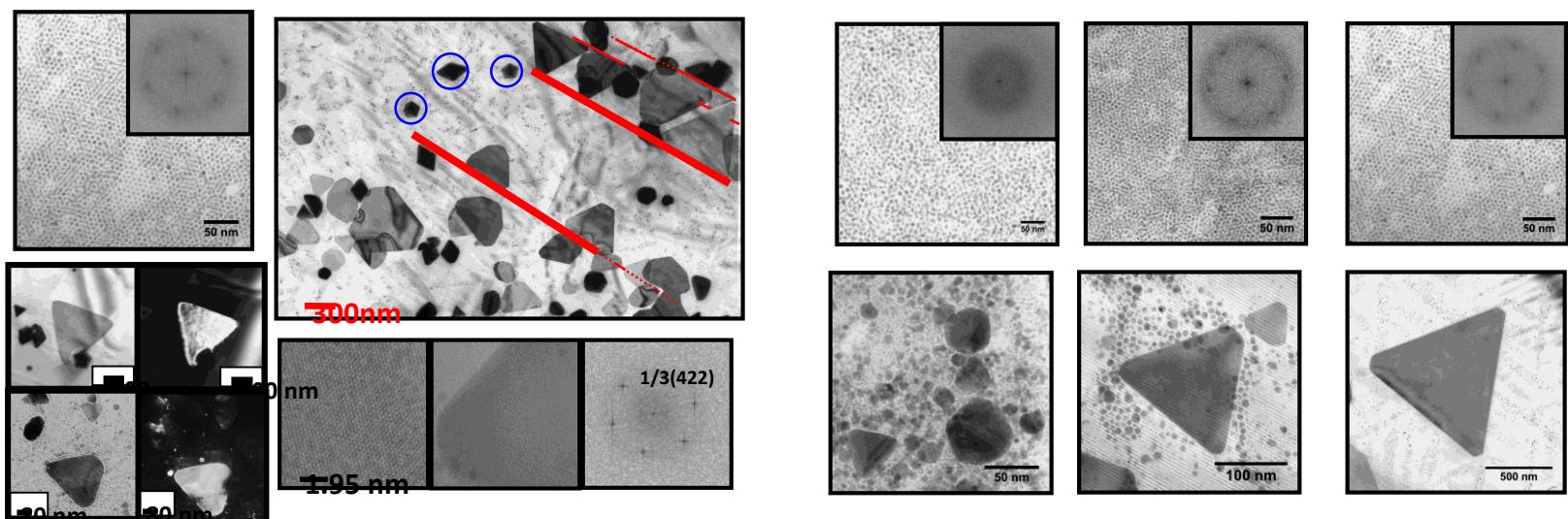
**Nanocristallinité: Cristallinité des nanomatériaux ( ordre des atomes dans une nanoparticule)**

**Supracristaux: assemblage cristallin à 3D de nanocristaux (ordre cristallin des nanocristaux)**

**Propriétés intrinsèques dues à l'autoassemblage cristallin de nanocristaux.**

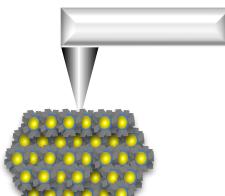
**Analogies entre les supracristaux et les cristaux atomiques.**

# Propriétés intrinsèques : La taille des triangles dépend de la longueur de cohérence des supracristaux.



Semblage à la croissance épithaxie produite par ultra à 300°C

# Elastic propriétés élastiques des supracristaux



Si Substrat

Mécanisme de (homogène/heterogène)

Depends on:

La Nanocrystallinité

→ SCs hydrophobes

→ SCs hydrophiles

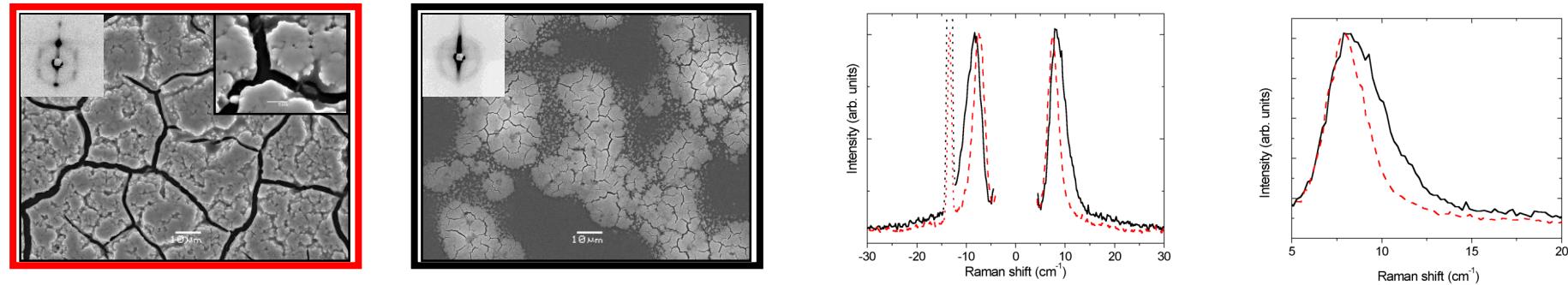
Agent protecteur

SCs hydrophobes

SCs hydrophile

	GPa	Au <sub>5</sub>	Au <sub>6</sub>	Au <sub>7</sub>	Au <sub>8</sub>
Film	0.24±0.18	0.1±0.06	0.09±0.05	0.08±0.04	
supracristaux	5.1±1.4	3.2±0.87	1.8±0.55	0.71±0.38	
	GPa	Co <sub>7</sub>	Co <sub>8</sub>	Co <sub>9</sub>	
Film/forme	0.74±0.40	0.74±0.40	0.74±0.40	0.74±0.40	
	GPa	SD Au <sub>5</sub>	polyAu <sub>5</sub>	Co <sub>7-e</sub>	Co <sub>7-HCP</sub>
Film	1.10±0.37	0.03±0.01	0.09±0.05	6.6±1.5	
	GPa	SD Au <sub>Mix</sub>	Poly Au5		
Film	0.55±0.16	0.025±0.09			
	GPa	SDAu <sub>5</sub> (hydrophobic)	SD Au <sub>(5)</sub> (hydrophilic)		
Film		0.315±0.15	0.55±0.16		

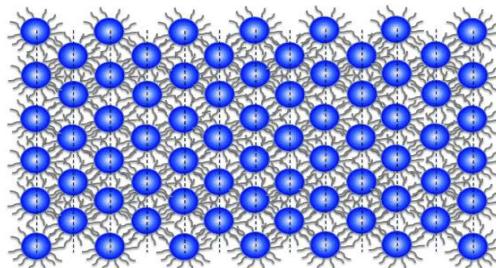
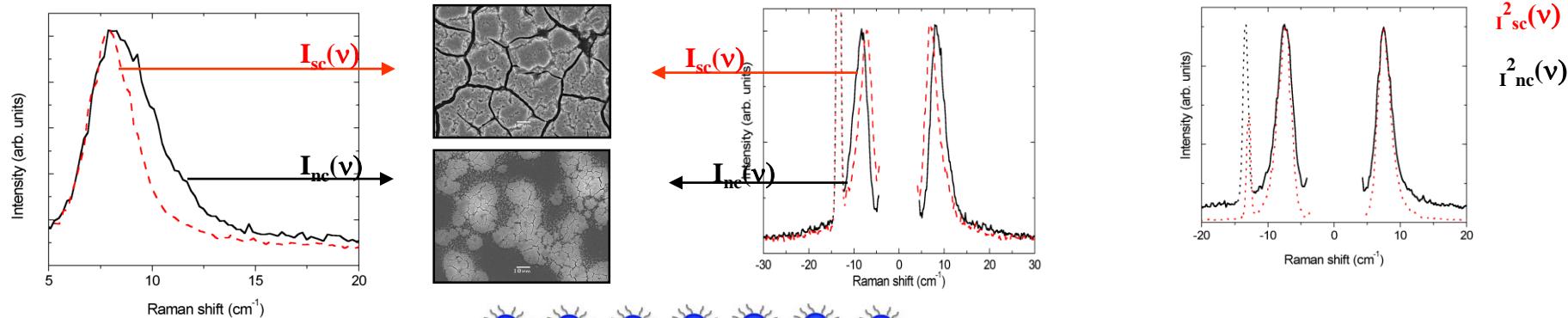
# Propriétés collectives physiques: Coherence entre nanocristaux dans un supracristal



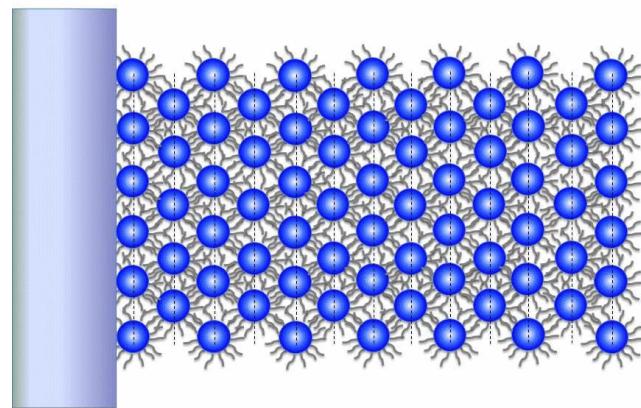
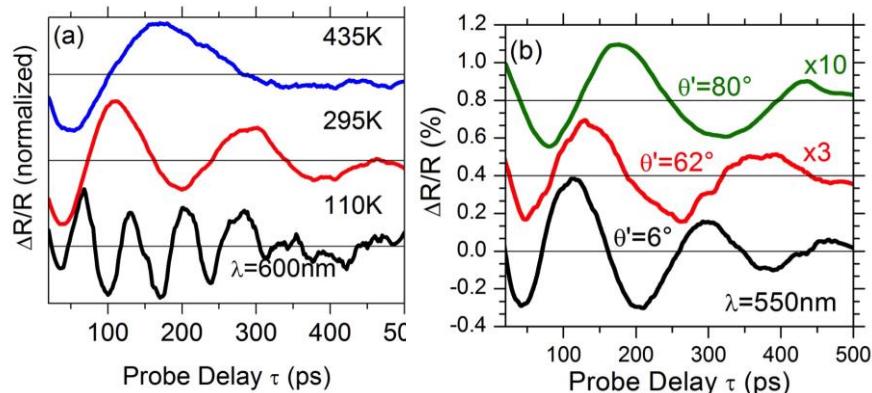
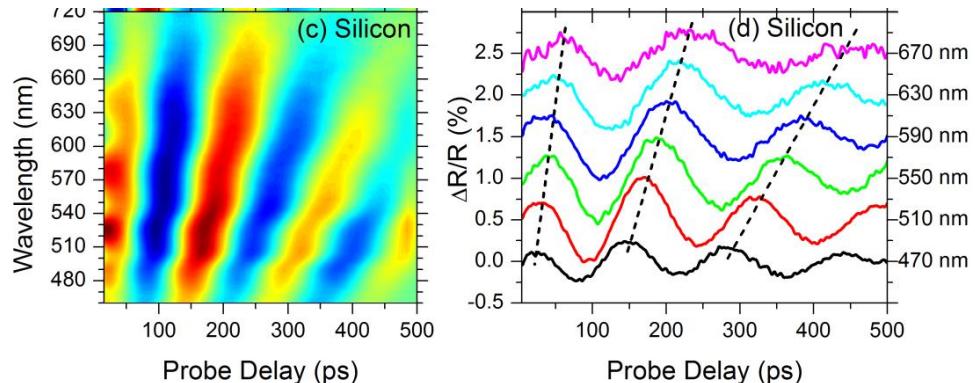
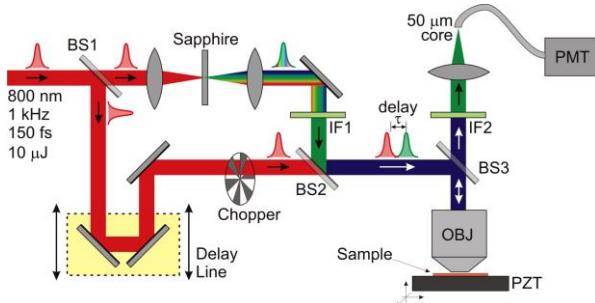
model

$$I_{sc}^{(s)}(\eta) \propto I_{nc}^2(\eta)$$

$$I_{sc}^{(s)}(\eta) \propto [L_{SD}(\eta)]^2$$



# Propriétés collectives physiques:: Onde propagative

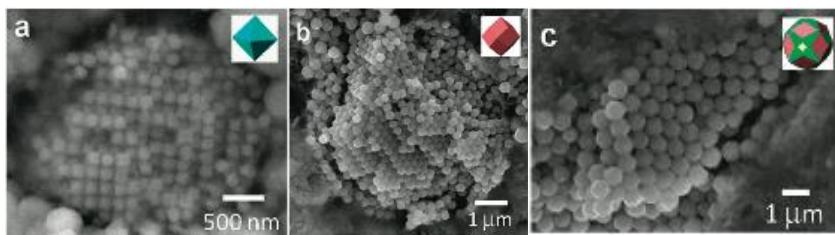


$$T = \frac{\lambda_{pr}}{2v_s \cdot n \cdot \cos \vartheta'} = \frac{\lambda_{pr}}{2v_s \cdot \sqrt{(n^2 - \sin^2 \vartheta)}}$$

# Analogies entre supracristaux et cristaux atomiques

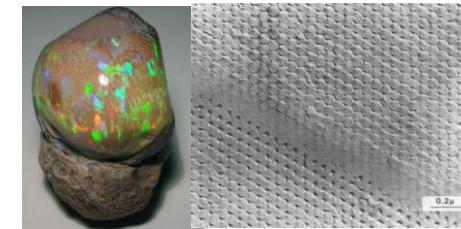
Atomes sont remplacés par des incompressibles nanocristaux et les liaisons atomiques par les chaines hydrocarbonées

Auto assemblage de  $\text{Fe}_3\text{O}_4$  microcristaux

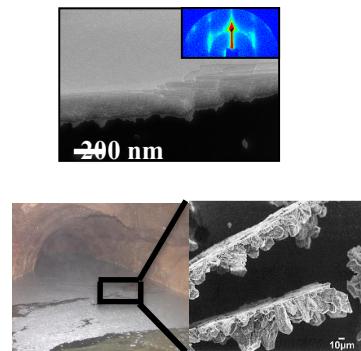
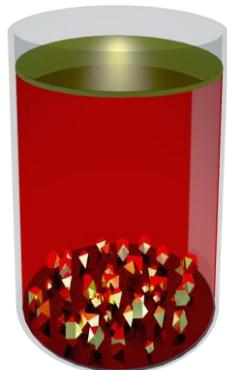


Nozawa, J.; Tsukamoto, K.; van Enckevort, W.; Nakamura, T.; Kimura, Y.; Miura, H.; Satoh, H.; Nagashima, K.; Konoto, M. *J. Am. Chem. Soc.* **2011**, *133*, 8782-8785.

Auto assemblage de microparticules de silice

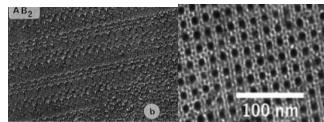


Sanders, J. V. *Nature* **1964**, *204*, 1151-1153.

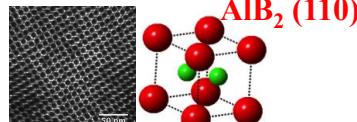


Goubet N., Portalès H., Cong Y., Arfaoui I., Albouy P.A., Mermet A. and Pileni M.P. *J. Am. Chem. Soc.*, **134**, 3714-3719, (2012)

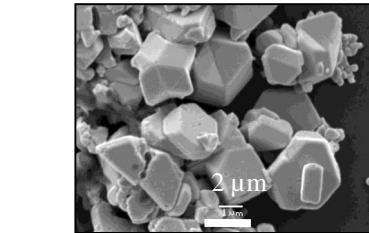
Minéral binaire



Supracristal binaire

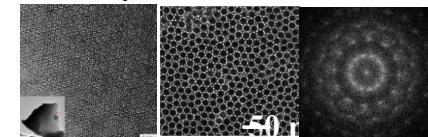


Z. Yang, J. Wei, P. Bonville, M.P. Pileni *Adv. Funct. Mater.*, **25**, 4908- (2015)

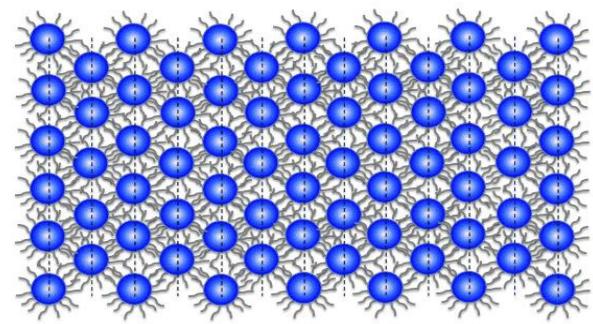
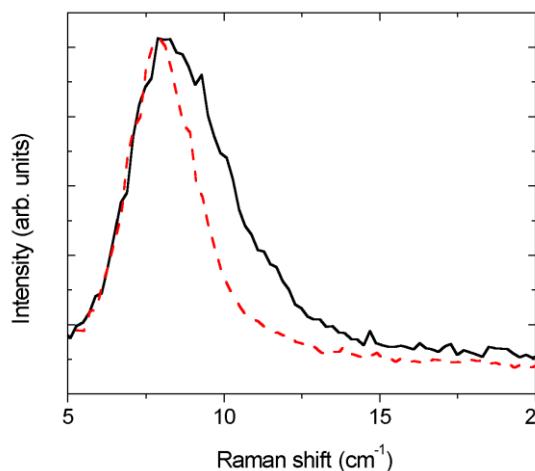
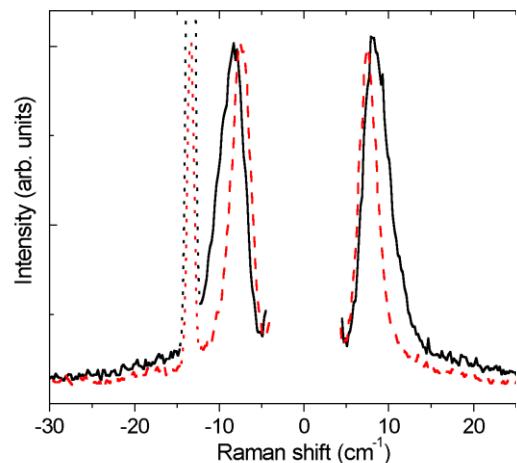


N.Goubet., H. Portalès., C.Yang., I. Arfaoui., P.A. Albouy , A. Mermet and M.P.. Pileni *J. Am. Chem.Soc.*, **134**, 3714-3719, (2012),

Quasicrystal      Quasi supracrystal

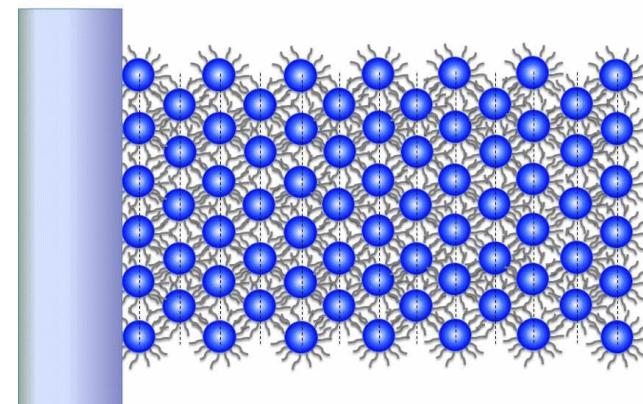
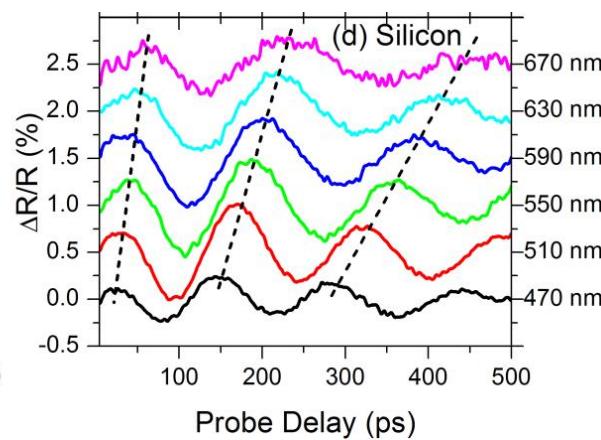
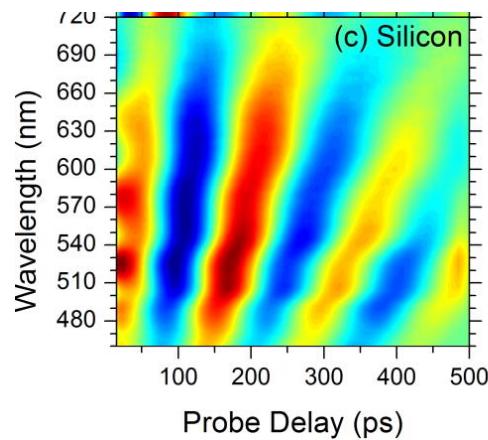


J. Wei, N. Schaeffer and M. P Pileni *J. Am. Chem. Soc.*, **137**, 14773-14784 (2015)  
Z. Yang, J. Wei, P. Bonville, M.P. Pileni *J. Am. Chem. Soc.* **137**, 4487-4493 (2015)



Courty, A. Mermet, P.A. Albouy, E. Duval and M.P. Pileni Nature Materials 4, 395-398 (2005), Phys. Rev. B 72, 85439, (2005),

### Propagation longitudinale dans un film fin de supracrystal de Co



I. Lisiecki, V. Halte, C. Petit, M.P. Pileni, J.Y. Bigot Advanced Material 20, 1-4, (2008)

I. Lisiecki, D. Polli, E. Duval, G. Cerullo and M.P. Pileni, Nanoletter 13, 504-508 (2013)