Auto-organisation de nanocristaux d'argent: Emergence de nouvelles propriétés physiques

Alexa Courty
UMR LM2N
Enseignant chercheur UPMC depuis septembre 1998

JAC 2011
3 février 2011

Les Nanomatériaux : Une histoire très ancienne

On trouve des nanoparticules d'or dans les mosaïques des romains, ces particules permettaient de colorer le verre.

Au moyen âge la couleur de certains vitraux d'église était due à des nanoparticules fabriquées involontairement lors de recuits thermiques des verres
Le rouge et le bleu étaient obtenus avec des nanoparticules d'or et d'argent.

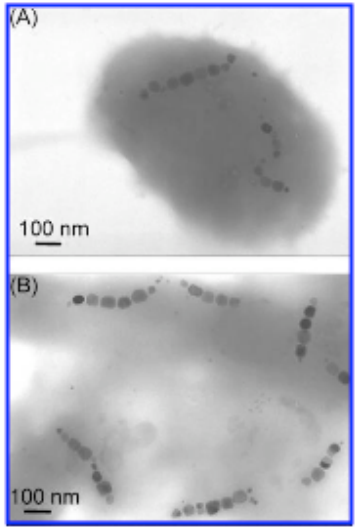
On retrouve des nanoparticules dans les teintures qu'utilisaient les égyptiens pour leurs cheveux

Vitrail église de Soisson

Flacon à parfum

Les Nanomatériaux : Une histoire très ancienne
La nature l'a fait avant….

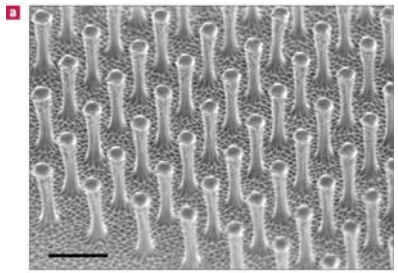
Nanoparticules magnétiques à l'état naturel:
Images MET d'un échantillon contenant des bactéries magnétotactiques déposées sur une grille de carbone



Migration des oiseaux (compas interne): les oiseaux sont sensibles au champ magnétique grâce aux **particules de magnétites présentes dans leur cerveau**

Effets liés à la taille nanométrique sont fréquents dans la nature:

L'effet "GECKO" Des poils microscopiques, tapissés de milliers de spatules d'environ 200 nm de largeur tapissent le dessous des pattes des geckos. Ces spatules peuvent s'approcher d'une surface à des distances nanométriques. À ces distances, il existe des forces, des liens entre les molécules, très faibles mais « très nombreux ». Ils s'additionnent et permettent au gecko d'évoluer sur des surfaces lisses verticales et même au plafond ! *(échelle 2µm)*



Quelques applications

Chaussettes antibactériennes
Les mauvaises odeurs sont dues à l'activité des bactéries. Pour y faire face, des nanopoudres de nitrate d'argent ont été intégrées à cette paire de chaussettes.
L'argent est un métal naturellement antibactérien qui, réduit en nanopoudres, est encore plus actif. Finies les mauvaises odeurs !

Jrnanotech
(www.jrnanotech.com)

Les crèmes solaires
contiennent du dioxyde de titane nanométrique

Raquette de tennis en nanotubes de carbones
Fabriquée avec des nanotubes de carbones, cette raquette est d'une grande légèreté tout en étant plus solide et plus flexible que les raquettes traditionnelles.

Babolat (www.babolat.com)

Vitrail
De nombreux vitraux d'églises ou de cathédrales de l'époque médiévale et moderne tirent leurs teintes rouge et bleue de nanoparticules d'or ou d'argent, contenues dans le verre.

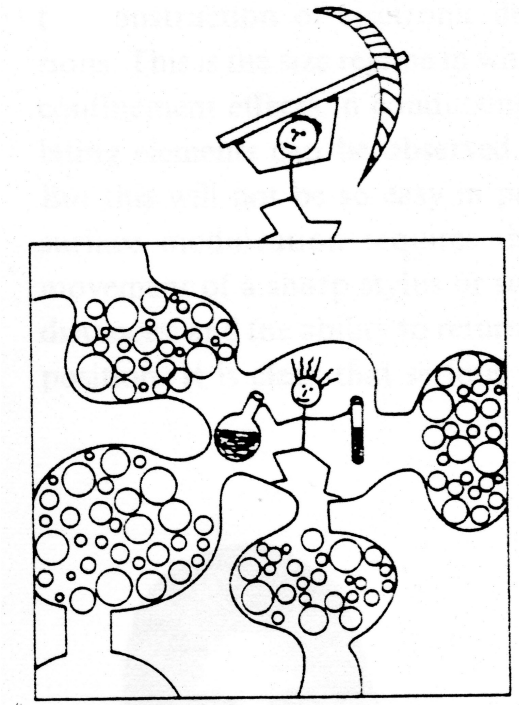
Oeuvre originale de Valérie Fortis

Méthodes d'élaboration des nanomatériaux:

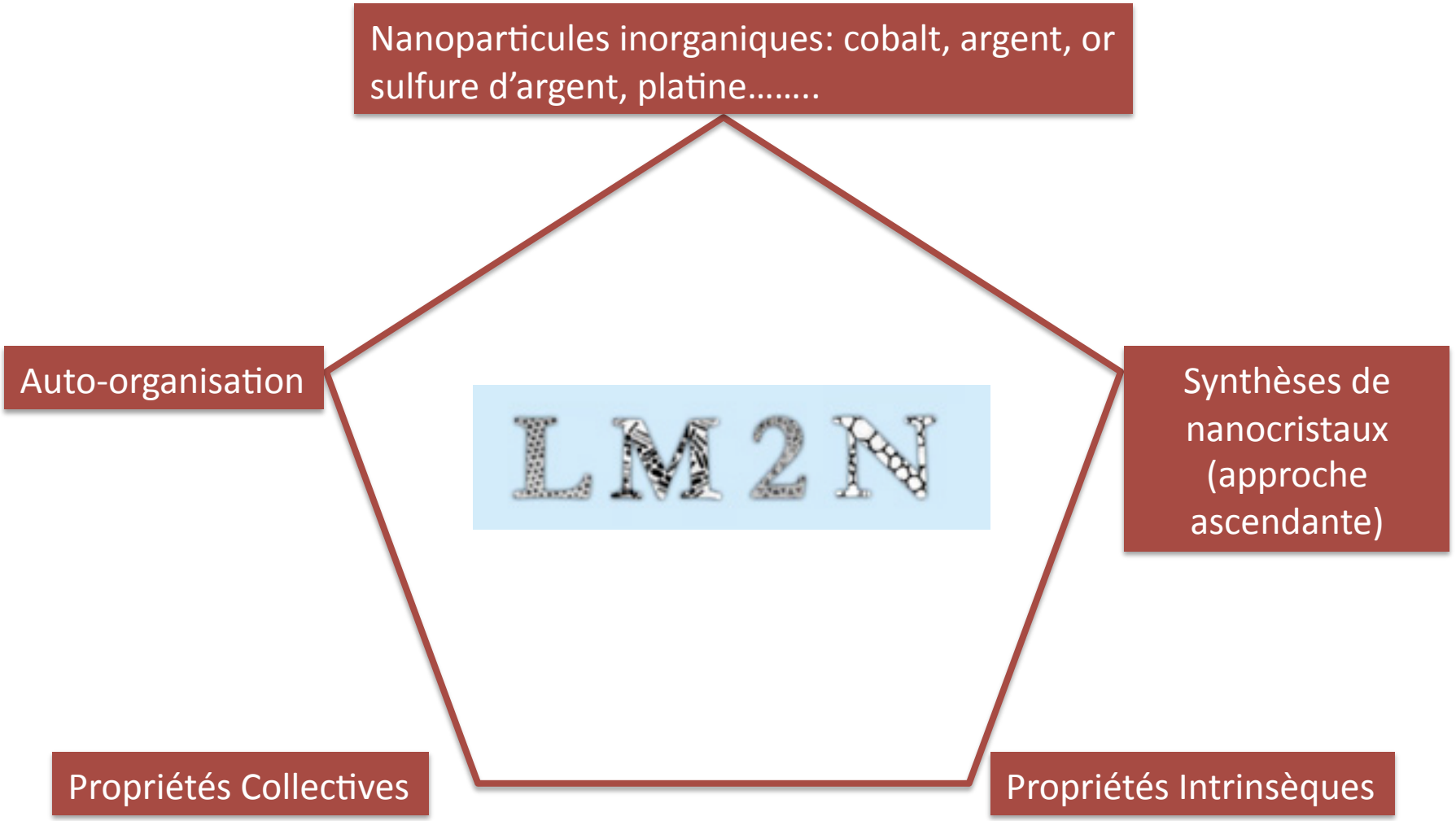
Deux approches dites:

Descendante (en anglais "top down"): consiste à diviser un matériau macroscopique à l'état massif en ses composés de tailles nanométriques.
Méthodes essentiellement physiques: broyage, ablation par arc électrique et par laser etc

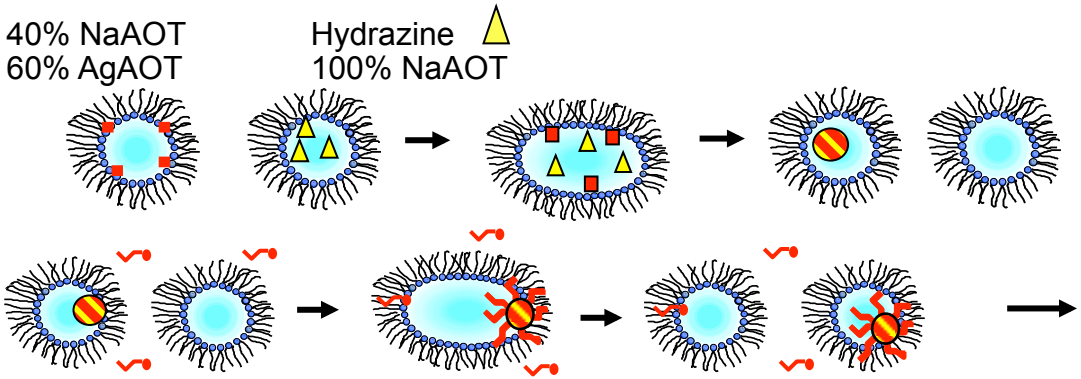
Ascendante (en anglais "bottom-up"): consiste à réaliser des nanomatériaux à partir d'atomes ou de molécules et à les auto-assembler.
Méthodes essentiellement chimiques: synthèse par transfert de phase liquide liquide, en micelles inverses, approche organométallique etc



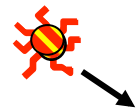
Nanochemistry and nanophysics compared.


Nanoparticules inorganiques: cobalt, argent, or sulfure d'argent, platine……..
Auto-organisation
LM2N
Synthèses de nanocristaux (approche ascendante)
Propriétés Collectives
Propriétés Intrinsèques

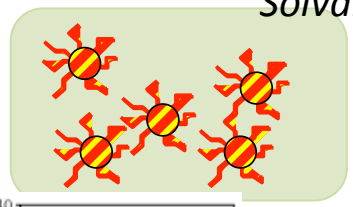
Nanocristaux d'argent: synthèse en micelles inverses



- Temps de réduction= 1 nuit
- habillage = dodecanethiol/decanethiol ($Ag\text{-}C_{12}/AgC_{10}$)
- Extraction
- Sélection en taille
- Dispersion = hexane/decane

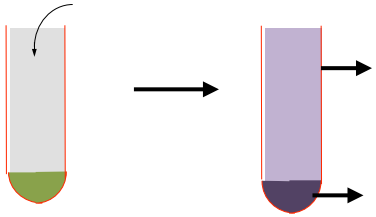


Solvant apolaire



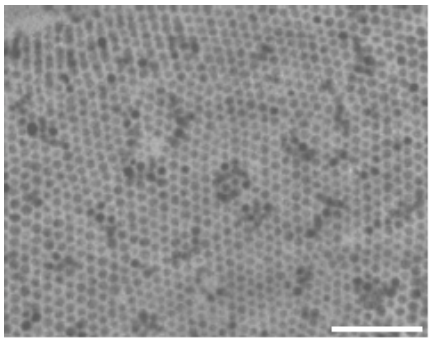
Mauvais solvant

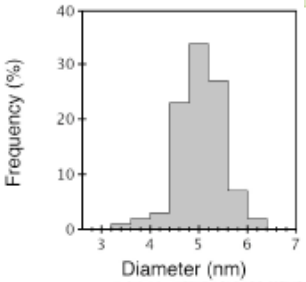
Selection en taille



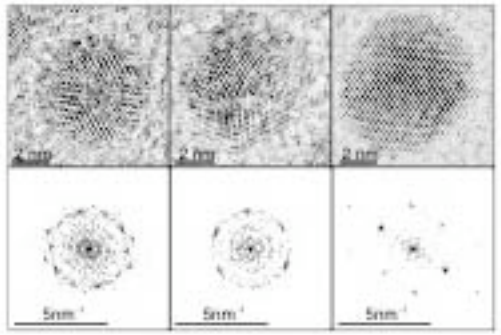
surnageant
Petites particules

précipité
Particules de grandes tailles

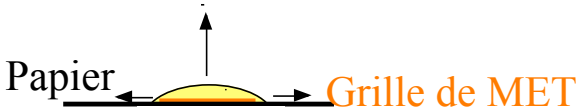




Diamètre moyen D= 5.0 nm
Distribution de taille 12%

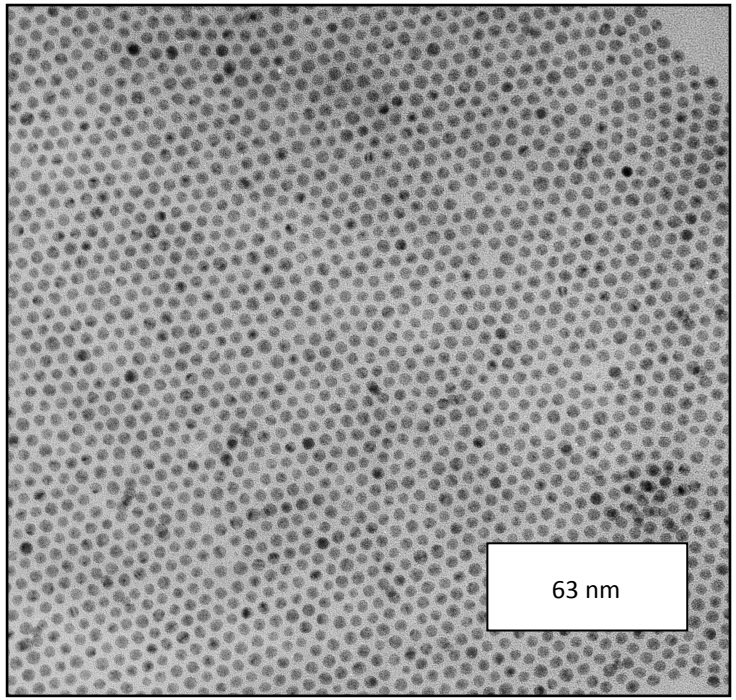


Dépôt de goutte

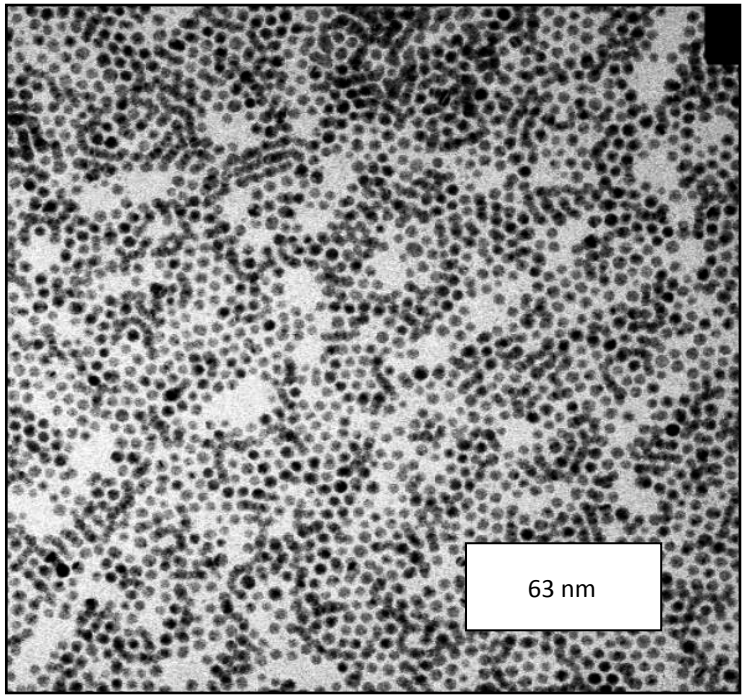


A. Taleb ; C. Petit; M.P. Pileni, *Chem Mater.* 9, 950-959; (1997) A. Courty, I. Lisiecki and M.P. Pileni, J.Chem.Phys, 116, 8074 (2002)

Influence du substrat sur l'organisation des nanocristaux



HOPG
Organisation sur longue distance

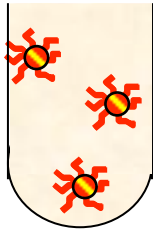


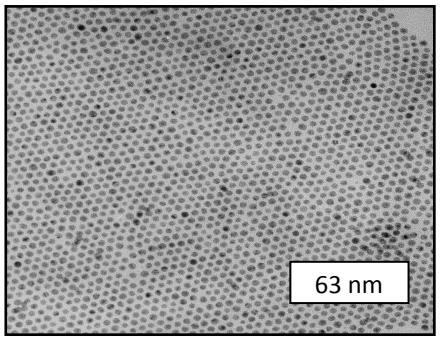
Carbone Amorphe
Organisation locale

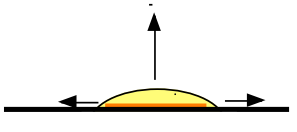
M.P. Pileni, Y. Lalatone, D. Ingert, I. Lisiecki and A. Courty, *Faraday Discussion 125, 251- (2004).*

Influences de la concentration et du mode de dépôt sur l'organisation à 2D et à 3D des nanocristaux d'argent

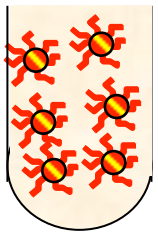
Solution diluée

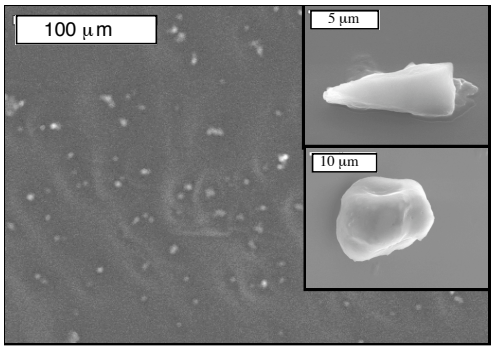


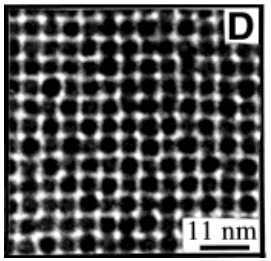


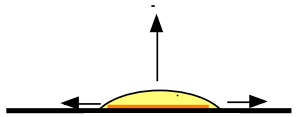


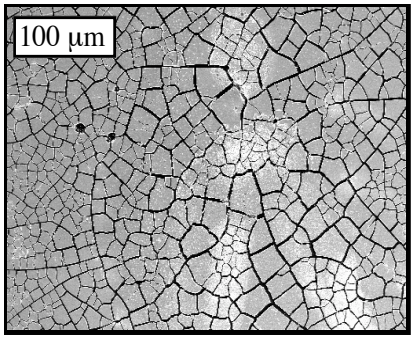
Solution concentrée

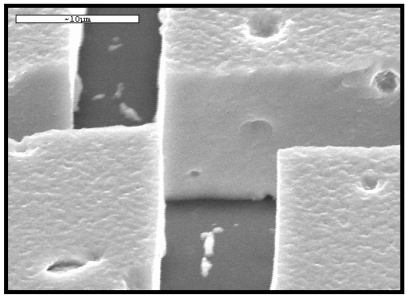


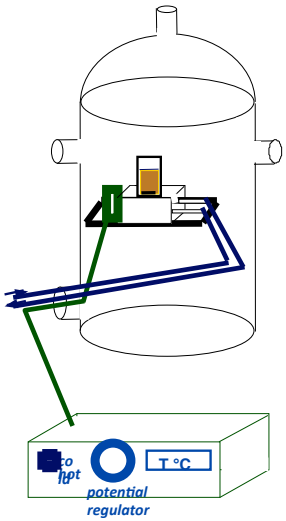












A.Courty, C. Fermon, and M.P. Pileni Adv. Mater. ; 13, 254, (2001), A. Courty, O. Araspin , C. Fermon and M.P. Pileni Langmuir, 17, 1372, (2001)

Contrôle de la structure cristalline des asssemblages 3D de nanocristaux d'argent

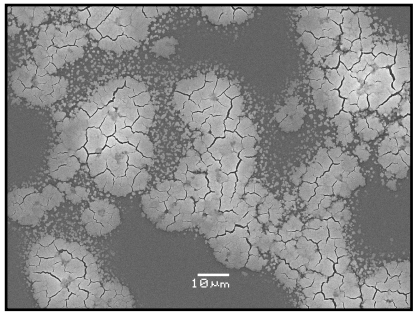
Ag-C12

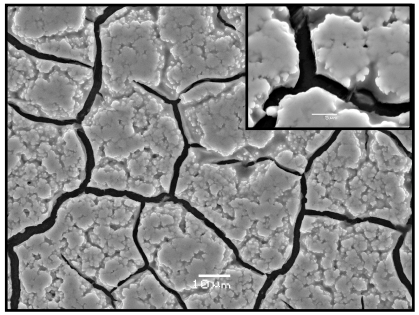
hexane

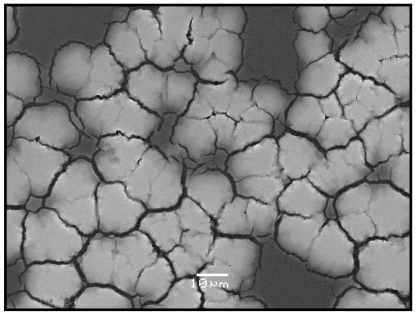
HOPG

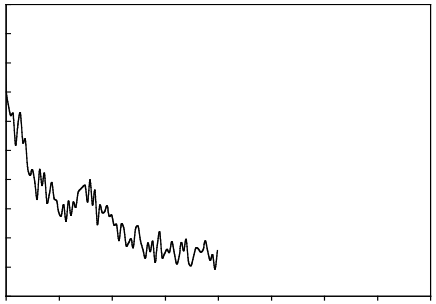
Temperature du substrat → **T°C**

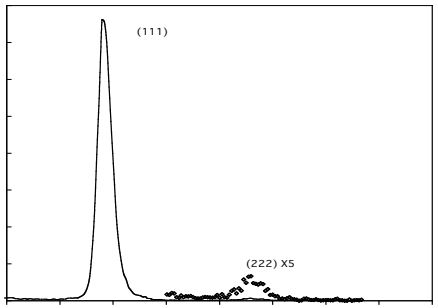
10°C | **22°C** | **35°C**

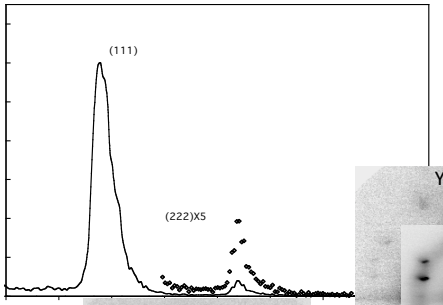


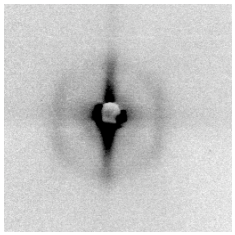


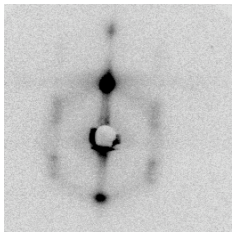


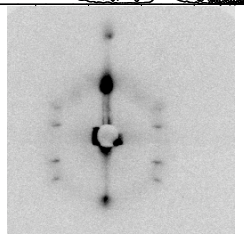


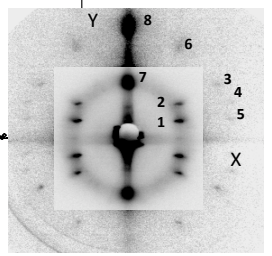












Indices h. k. l	q_x(meas.) Å^{-1}	q_x(calc) Å^{-1}	q_y(meas.) Å^{-1}	q_y(calc) Å^{-1}	d_{hkl}(meas.) nm	d_{hkl}(calc) nm
(1) 1.1.-1	0.0338	0.0324	0.0936	0.0918	6.31	6.45
(2) 2.0.0	0.0644	0.0649	0.0905	0.0918	5.65	5.60
(3) -1.3.1	0.0966	0.0974	0.1578	0.1590	3.39	3.37
(4) 1.1.3	0.1658	0.1623	0.0901	0.0918	3.33	3.37
(5) 2.2.-2	0.0644	0.0649	0.1803	0.1836	3.28	3.23
(6) 1.1.-3	0.0322	0.0324	0.1803	0.1836	3.43	3.37
(7) 1.1.1	0.102	0.0974	0	0	6.16	6.45
(8) 2.2.2	0.198	0.1948	0	0	3.17	3.22

A. Courty, A. Mermet, P.A. Albouy, E. Duval and M.P. Pileni, Nature Materials 4 (2005) 395

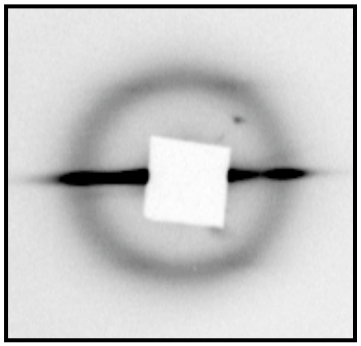
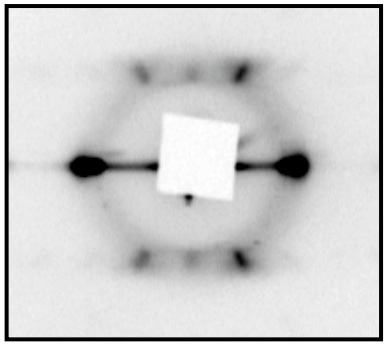
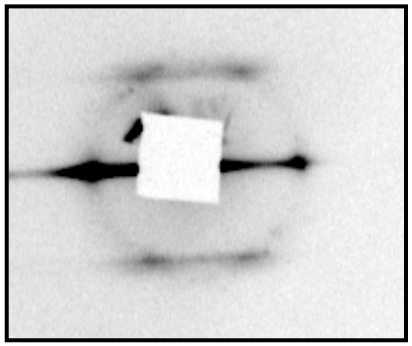
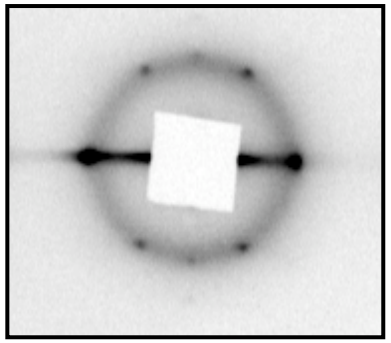
A. Courty, P.A. Albouy, A.Mermet, E.Duval and M.P. Pileni, J.Phys. Chem (2005)

Ag-C12

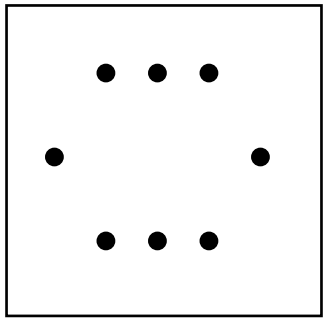
Contrôle de la structure cristalline des supracristaux de nanocristaux d'argent

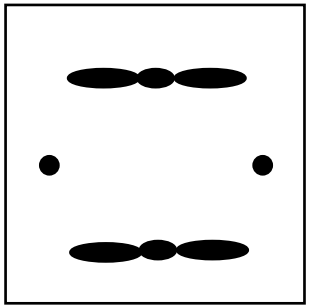
decane
HOPG

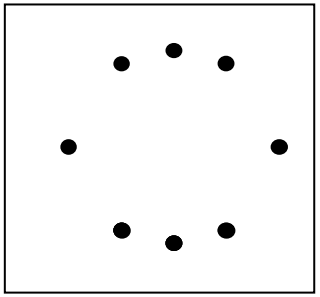
Temperature du substrat

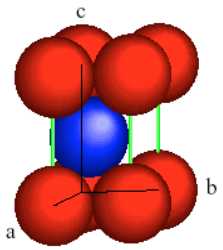
15°C	25°C	35°C	50°C	T°C
				
Amorphe	hexagonal compact	compact	cubique centré	

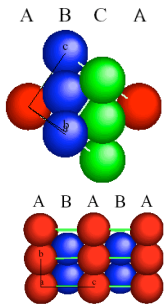
Influence de la température de dépôt

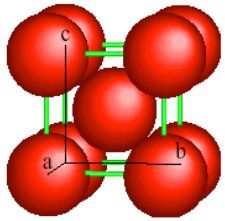










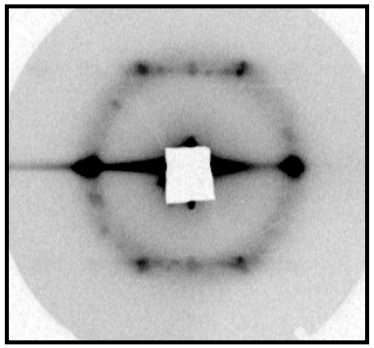
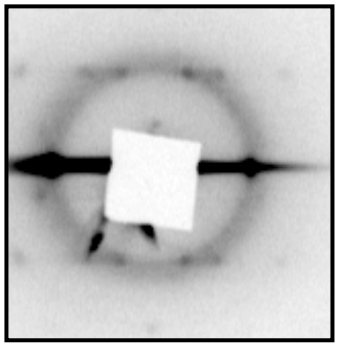
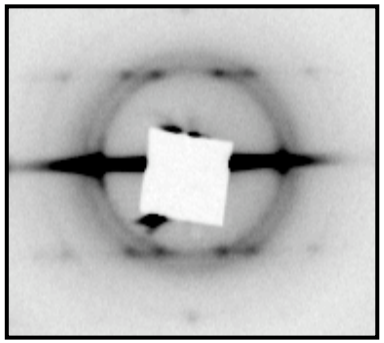
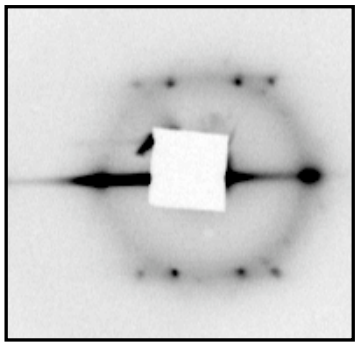
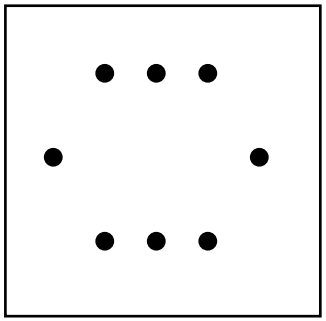
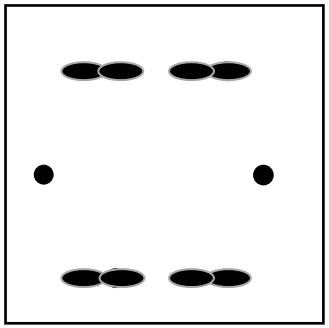
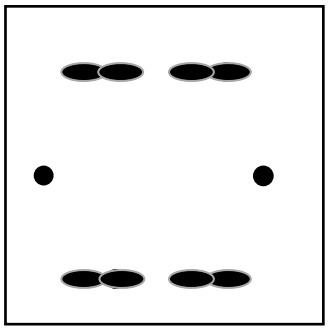
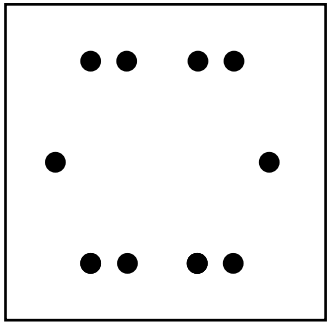
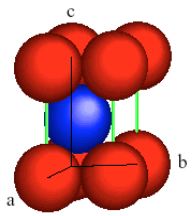
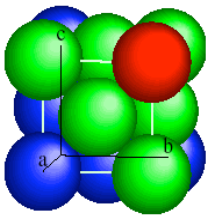
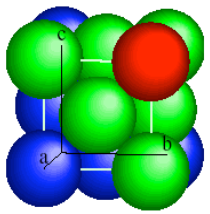


A.I.Henry, A.Courty, P.A.Albouy, J.Israelashivili, and M.P. Pileni Nanoletters 8, 2000 (2008) A.Courty, J.Phys.ChemC., 1114,3719, 2115, (2010).

Contrôle de la structure cristalline des supracristaux de nanocristaux d'argent

Ag-C10

Temperature du substrat

15°C	25°C	35°C	50°C	T°C
				
hexagonal compact	compact	cubique à face centrées	cubiqueà faces centrées	
				
				

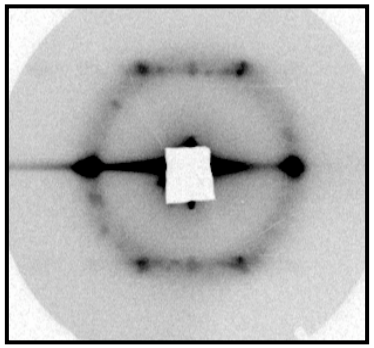
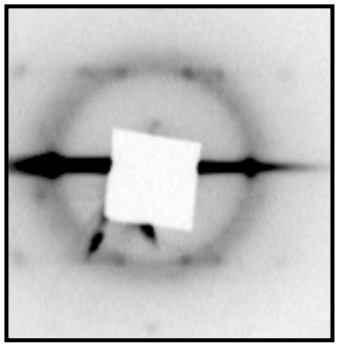
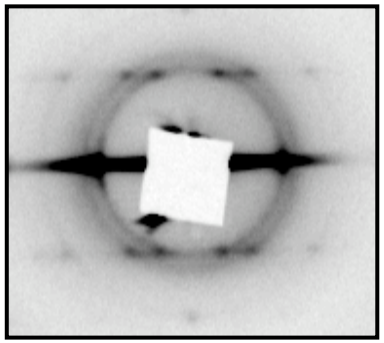
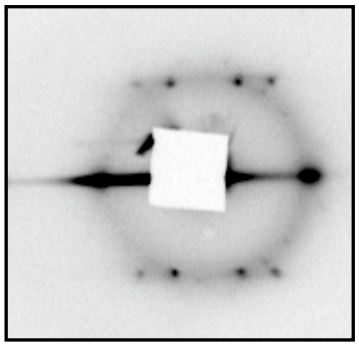
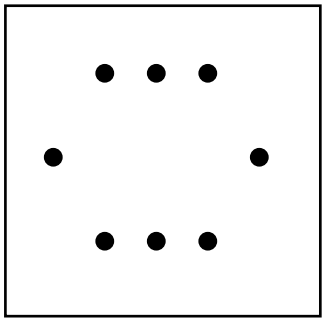
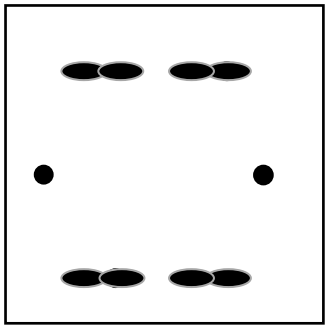
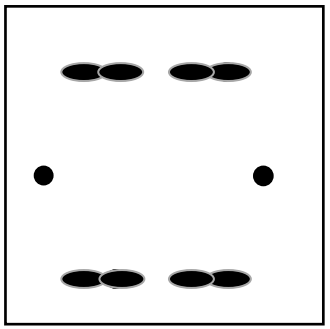
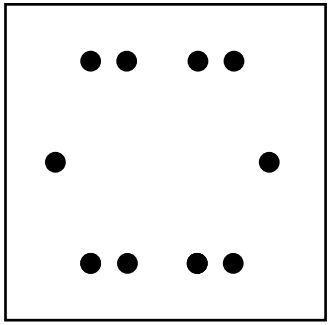
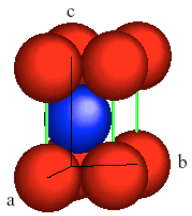
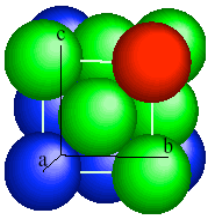
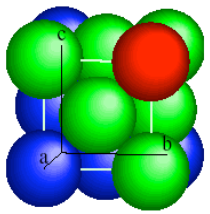
Influence de la longueur de la chaine alkyl et de la température de dépôt.

A.I.Henry, A.Courty, P.A.Albouy, J.Israelashivili, and M.P. Pileni Nanoletters 8, 2000 (2008) A.Courty, J.Phys.ChemC., 1114,3719, 2115, (2010).

Contrôle de la structure cristalline des supracristaux de nanocristaux d'argent

Ag-C10

Temperature du substrat

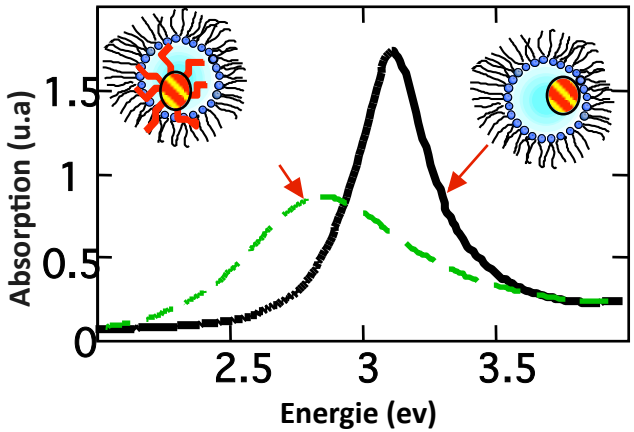
15°C	25°C	35°C	50°C	T°C
				
hexagonal compact	compact	cubique à face centrées	cubiqueà faces centrées	
				
				

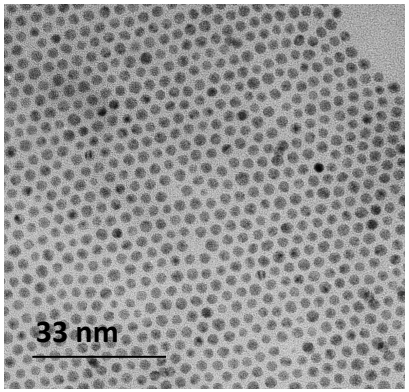
Influence de la longueur de la chaine alkyl et de la température de dépôt.

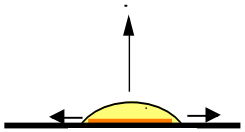
A.I.Henry, A.Courty, P.A.Albouy, J.Israelashivili, and M.P. Pileni Nanoletters 8, 2000 (2008) A.Courty, J.Phys.ChemC., 1114,3719, 2115, (2010).

Propriétés optiques collectives de nanocristaux d'argent organisés à 2D

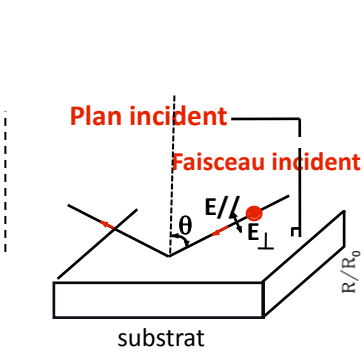
$$C = \frac{18\pi\varepsilon_m^{3/2}\varepsilon(\omega)}{\lambda((\varepsilon_1(\omega)+2\varepsilon_m)^2+\varepsilon_2(\omega)^2)}$$

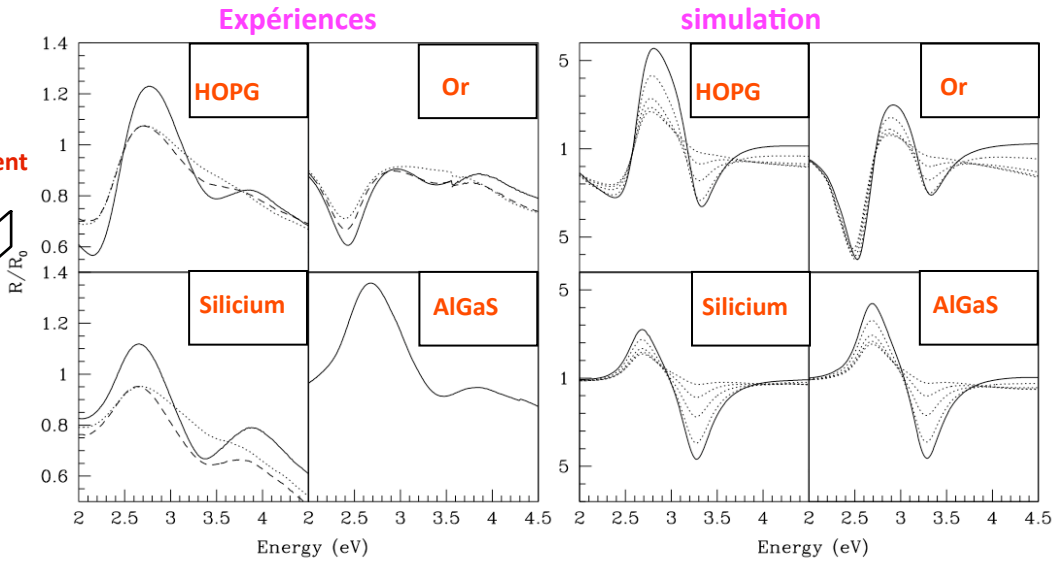


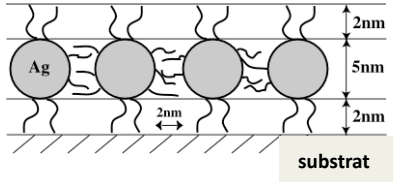


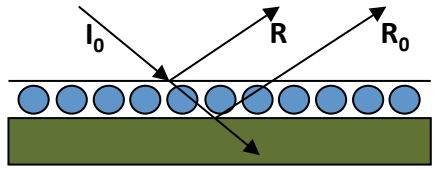


Spectres de réflectivité de nanocristaux d'argent déposés sur différent substrats



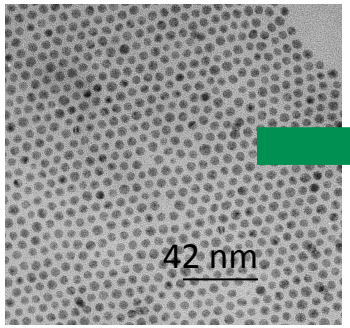


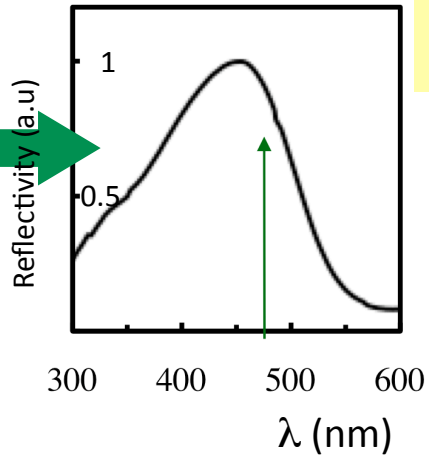




A.Taleb, V. Russier, A.Courty & M.P. Pileni Phys.Rev.B. 59, 13350 (1999)
N. Pinna, M. Millard, A. Courty, V. Russier & M. P. Pileni, Phys. Rev. B, 66, 45415 (2002)

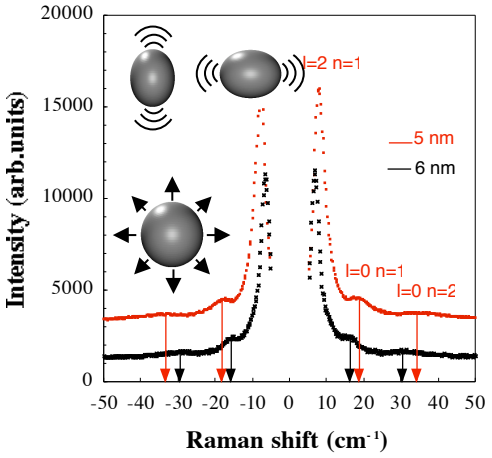
Cohérence vibrationnelle dans les nanocristaux d'argent: Expérience de diffusion Raman basse fréquence





Couplage Plasmon - Vibration

λ_{exc}=488nm



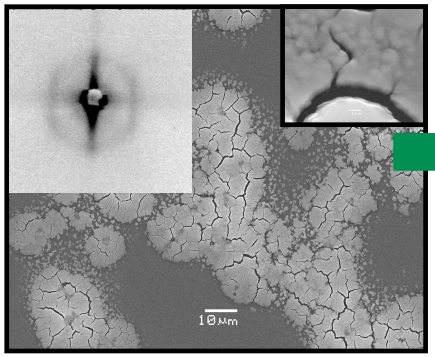
Spherical nanocrystals

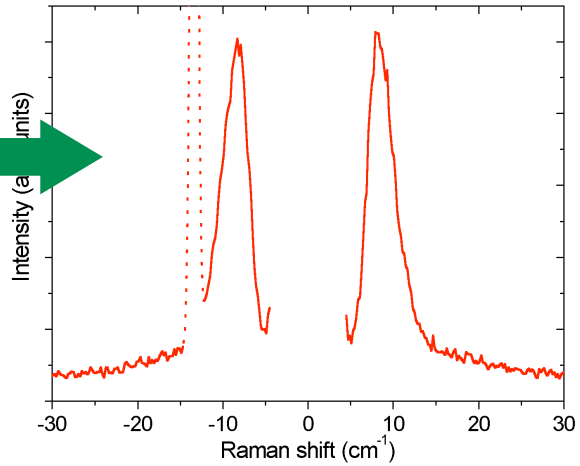
ν_T **transversal sound velocity**

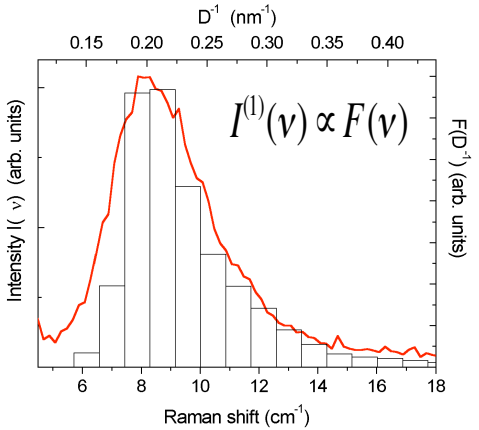
$S_{l,n} \alpha \nu_T / \nu_T$

$$\nu_{\ln} = \frac{S_{\ln} v_t}{D}$$

⇒ *Deposition on a HOPG substrate at 10°C*



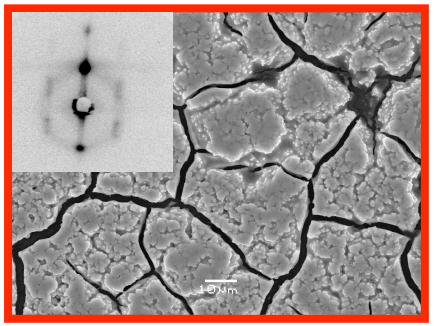




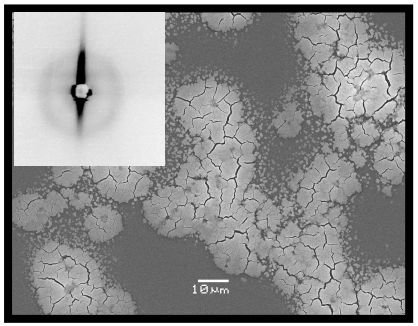
A. Courty, I. Lisiecki and M.P. Pileni, J.Chem.Phys, 116, 8074 (2002)

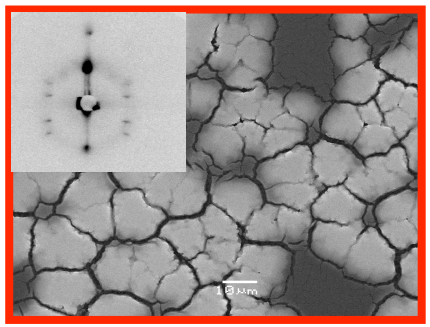
A. Courty, A. Mermet, P.A. Albouy, E. Duval and M.P. Pileni, Nature Materials 4 (2005) 395

Cohérence vibrationnelle dans des supracristaux cfc de nanocristaux d'argent: effet de taille

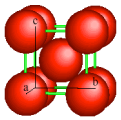


Supracristaux de petites tailles (<<$\lambda_{excitation}$)





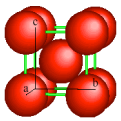
Supracristaux de grandes tailles (>$\lambda_{excitation}$)

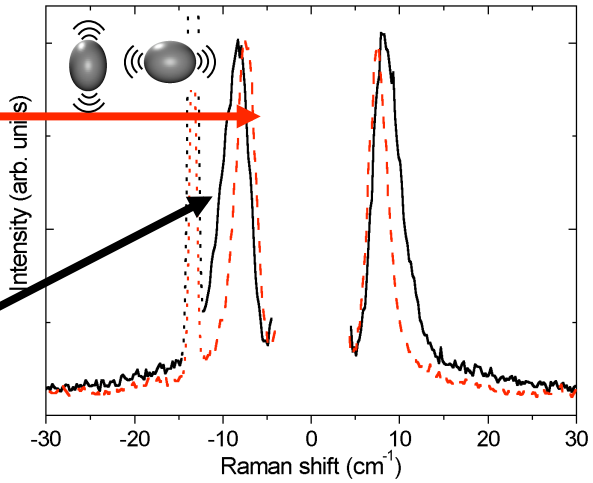


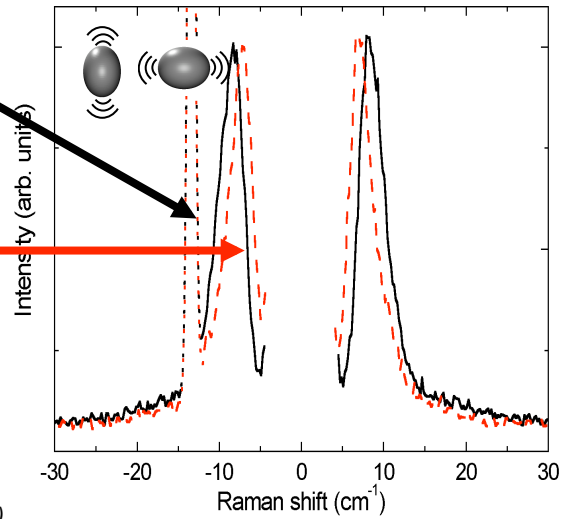
cfc

amorphe

cfc

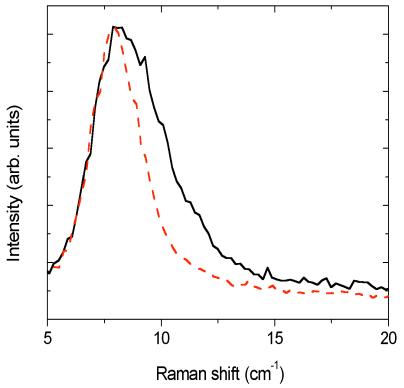




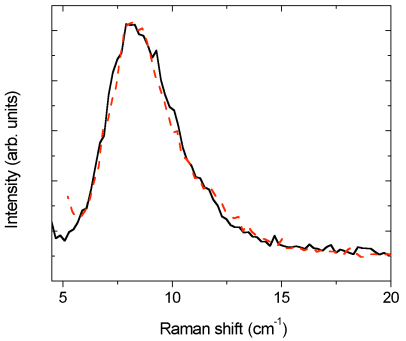


hexane

Ag-C12



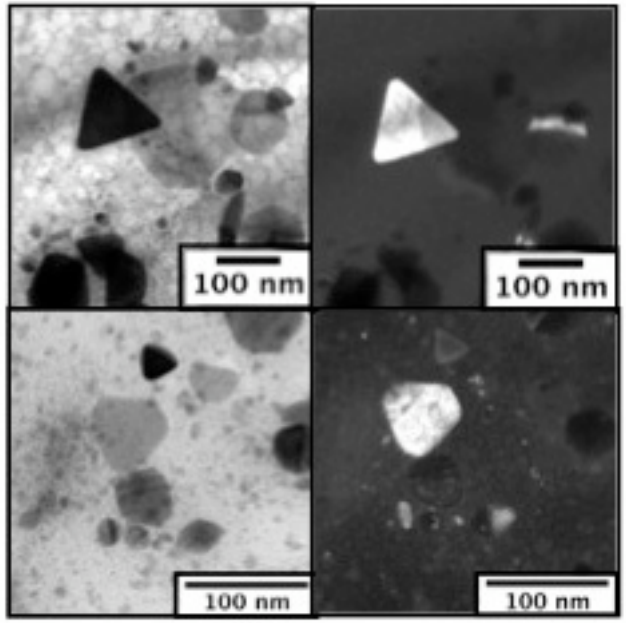
$$I_{sc}^{(s)}(\nu) \propto \left[L_{SD}(\nu)\right]^2 I_{nc}^2(\nu)$$

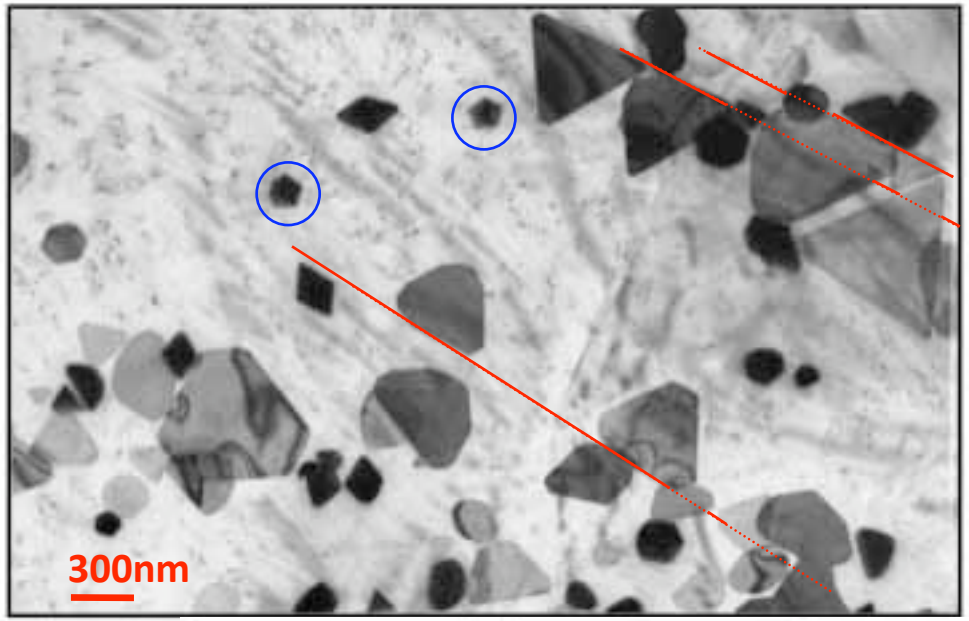


$$I_{SC}^{(l)}(\nu) \propto \left[L_{SD}(\nu)\right]^2 I_{nc}(\nu)$$

A.Courty, A. Mermet, P.A. Albouy, E. Duval & M.P. Pileni, Nature Materials 4, 395 (2005).
A.Courty, A. Mermet, P.A. Albouy, E. Duval & M.P. Pileni, J.Phys.Chem., 109, 2115, (2005).
E.Duval, A.Mermet, A. Courty, P.A. Albouy & M.P. Pileni, Phys. Rev. B, 72, 0854395 (2005).

Formation de triangles d'argent par coalescence induite par chauffage (50°C) d'organisations de nanocristaux d'argent

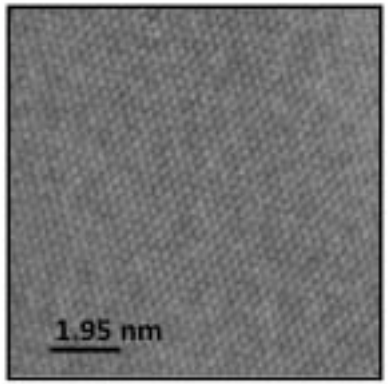


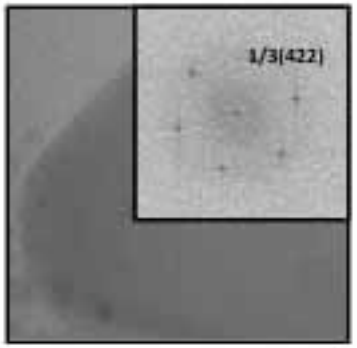


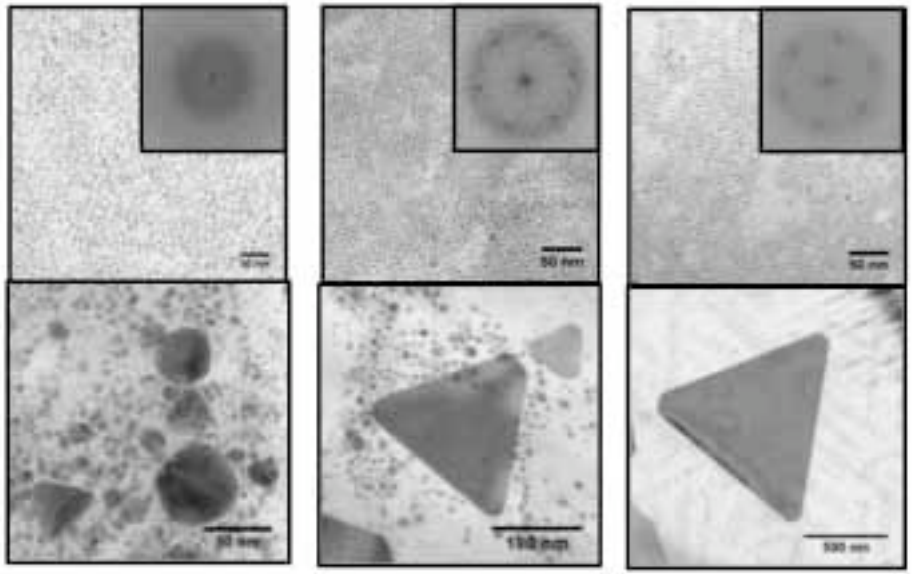
décane

HOPG

Ag-C10

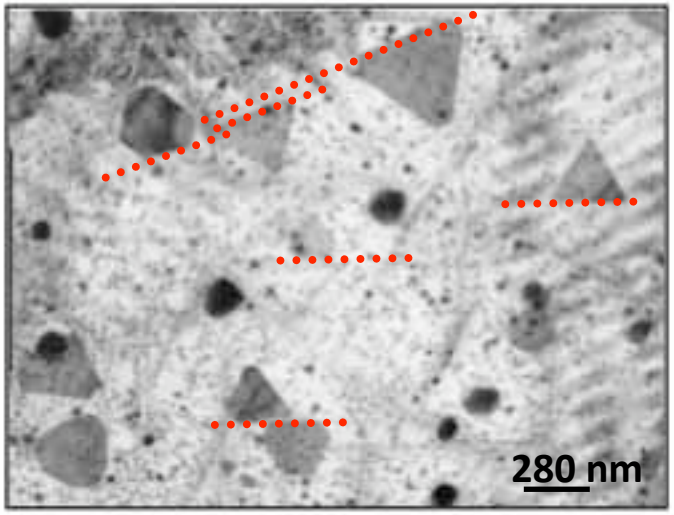






A.Courty, A.I. Henry, N. Goubet & M.P. Pileni, Nature Materials 6,900, (2007) and J.Phys.Chem.C, 112,48, (2008)

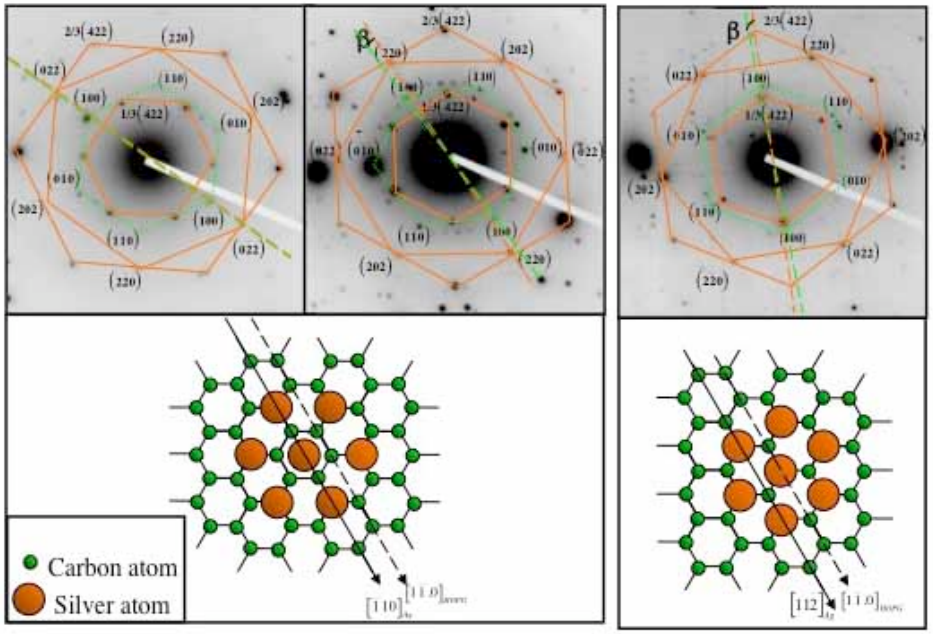
Formation de triangles d'argent par coalescence induite par chauffage (50°C) d'organisations de nanocristaux d'argent



décane

HOPG

Ag-C10

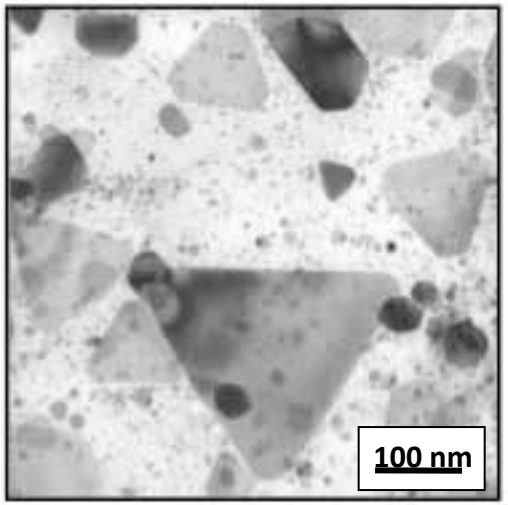


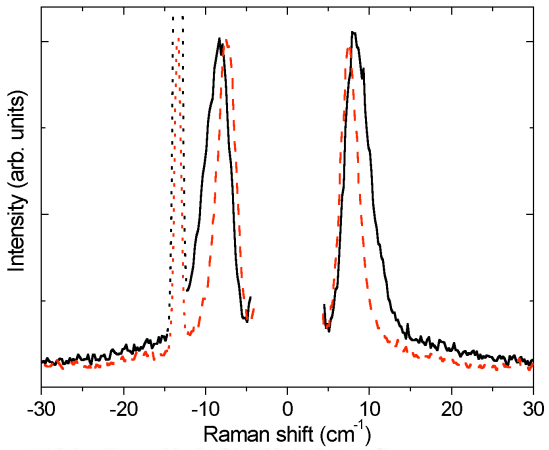
Une orientation epitaxiale majoritaire définie par : $[\bar{1}10]_{Ag}$ // $[1\bar{1}0]_{HOPG}$ $(111)_{Ag}$ // $(001)_{HOPG}$

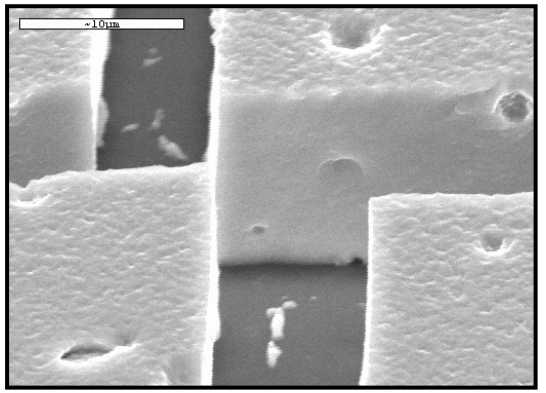
Une orientation epitaxiale secondaire $[11\bar{2}]_{Ag}$ // $[1\bar{1}0]_{HOPG}$ $(1\bar{1}1)_{Ag}$ // $(001)_{HOPG}$

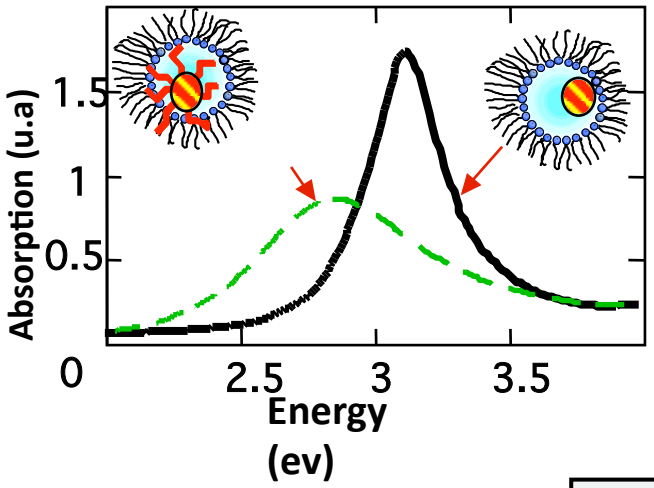
A. Courty, A-I. Henry, N. Goubet and M.P. Pileni, Nat.Mater (2007)

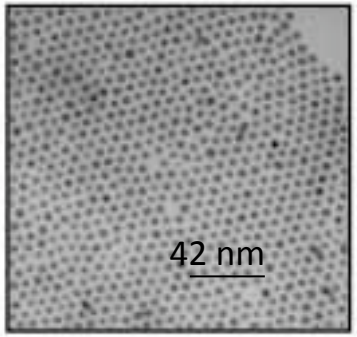
Conclusion

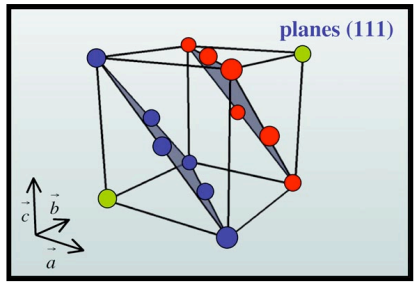

100 nm

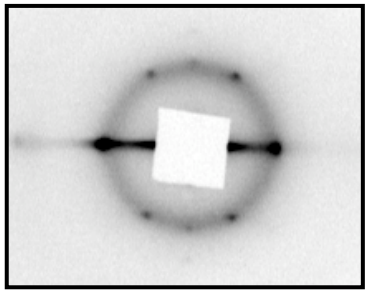

Intensity (arb. units)
-30
-20
-10
0
10
20
30
Raman shift (cm-1)

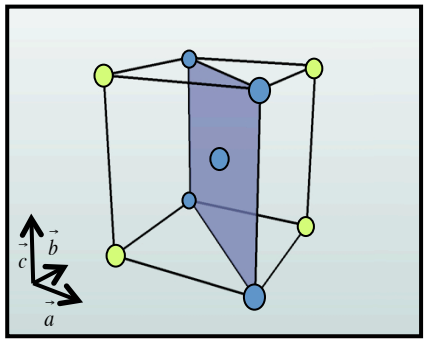


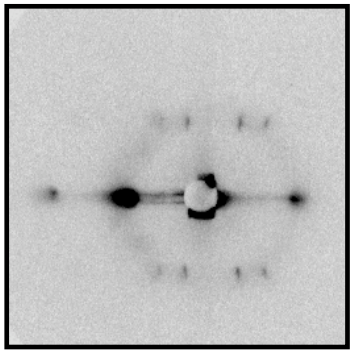

Absorption (u.a)
1.5
1
0.5
0
2.5
3
3.5
Energy
(ev)

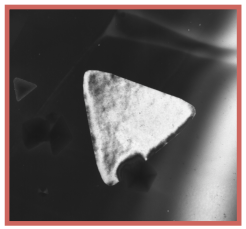

42 nm


planes (111)

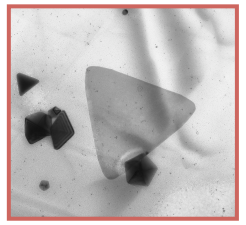








remerciements



- **Pr. Marie-Paule Pileni**
- **Dr. Isabelle Lisiecki**
- **Dr. Johannes Richardi**
- **Nicolas Goubet**

Laboratoire des Matériaux Mésoscopiques et Nanométriques (LM2N) Université Paris VI

- **Dr. Anne-Isabelle Henry, Dr. Mathieu Maillard, Dr. Nicolas Pinna**

- **Dr Pierre-Antoine Albouy** *Laboratoire de Physique des Solides (LPS), Université Paris XI*
- **PR Eugène Duval, Pr Alain Mermet,** *Laboratoire de Physico-Chimie des Matériaux Luminescents (LPCLM), Université Claude Bernad, Lyon*
- **Pr Jacob Israelachvili,** *Department of Chemical Engineering , University of California in Santa Barbara, USA*