

Synthèse et Propriétés Optiques de Nanoparticules Colloïdales et de Couches Minces Nanostructurées

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Palaiseau

Introduction

**Pourquoi fait-on des
Matériaux sol-gel et des nanoparticules
dans le groupe de chimie du solide ?**

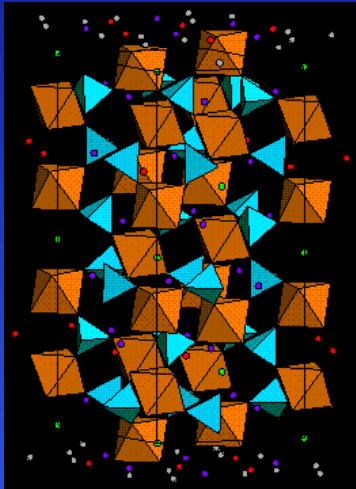
De l'alumine β aux gels de silice

(en prenant quelques raccourcis ...)

Cristaux



N
A
S
I
C
O
N



Ionic Superconductors of β -Alumina Type

R. Collongues, J-P. Boilot, P. Colomban, A. Kahn, J. Thery
Revue Intern. des Hautes Températures et des réfractaires 16 (2): 125-132 1979

Crystal Structure of the true NASICON - $\text{Na}_3\text{ZrSi}_2\text{PO}_{12}$

J-P. Boilot, G. Collin, P. Colomban
Materials Research Bulletin 22 (5): 669-676 (1987)

NASICON - Amorphous to Crystalline Compounds

J-P. Boilot, P. Colomban, G. Collin
Solid State Ionics 18-9: 974-980 (1986)

Formation of Superionic Gels and Glasses by low-temperature Chemical Polymerization

J-P. Boilot, P. Colomban, N. Blanchard
Solid State Ionics 9-10 639-643 (1983)

NMR Study of the Sol-Gel Polymerization

J-C. Pouxviel, J-P. Boilot, J-C. Beloeil, J-Y. Lallemand
Journal of Non-Crystalline Solids 89 (3): 345-360 (1987)

An Aluminosiloxane as a ceramic precursor

JC Pouxviel, J-P. Boilot, O. Poncelet, LG Hubert Pfalzgraf, A. Lecomte,
A. Dauger, J-C. Beloeil - Journal of Non-Crystalline Solids 93 (2-3): 277-286 (1987)

transitions de phases
Distorsions
Verres

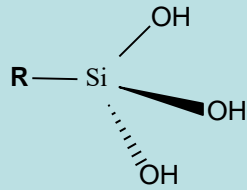
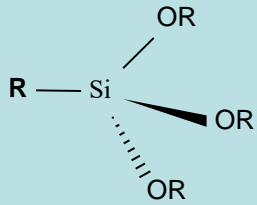


Polymerisation
Sol-Gel

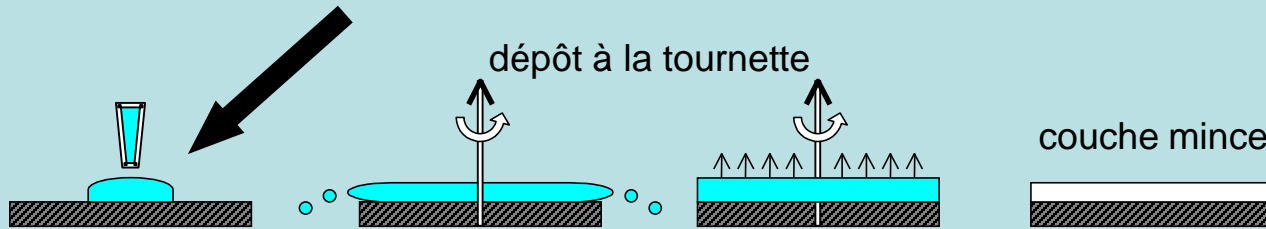
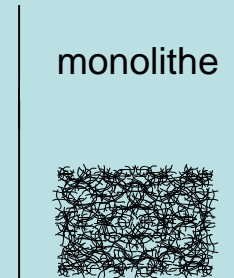
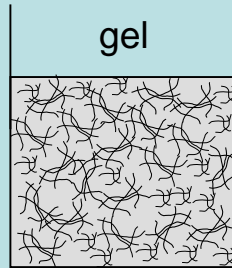
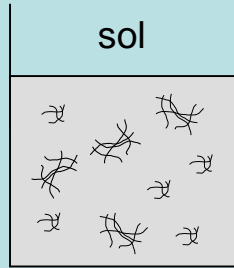
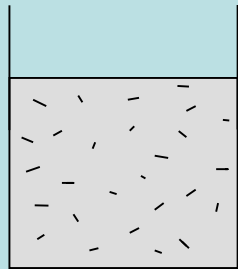
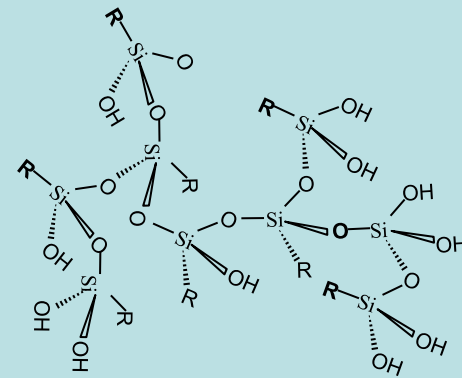
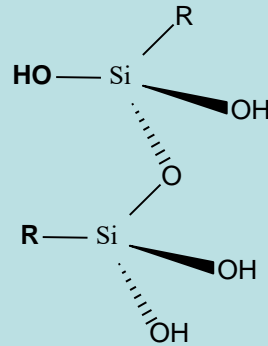
"The heat treatment of the gels leads, after removal of volatile siloxanes, to **transparent glass ceramics** with a molar composition of about 92% Al_2O_3 -8% SiO_2 "

Matrices de silice

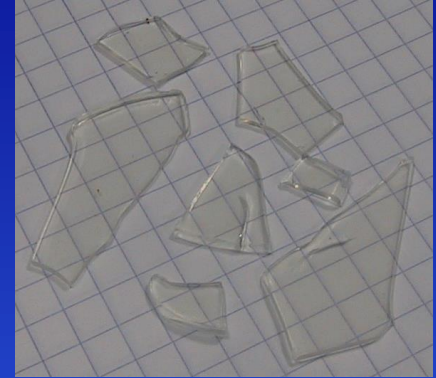
Alcoxyde de silicium hydrolyse



condensation



inorganique



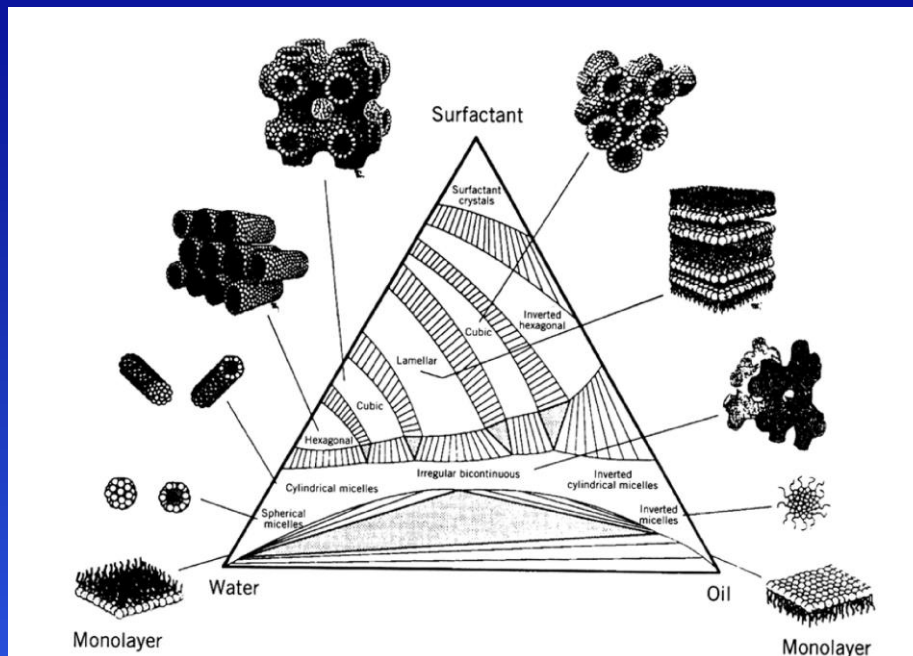
hybride



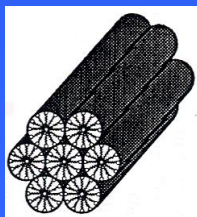
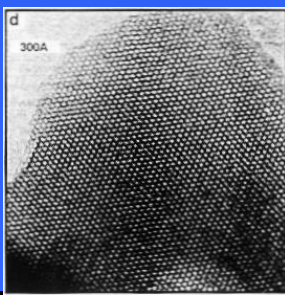
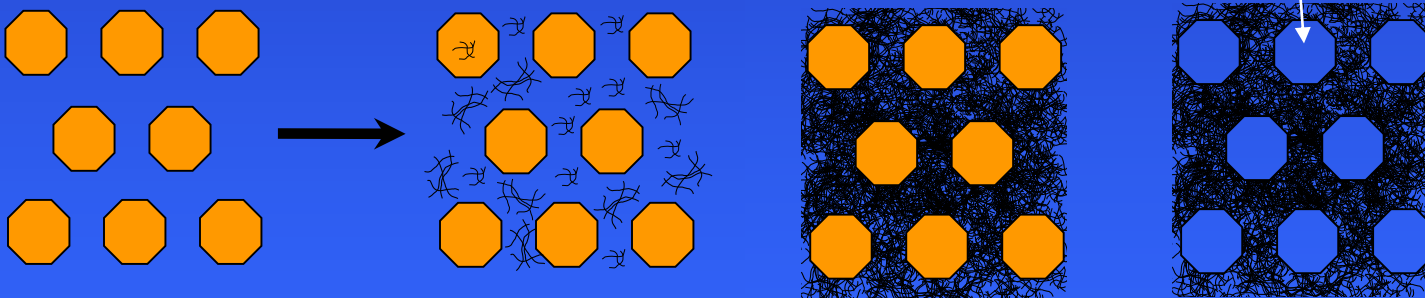
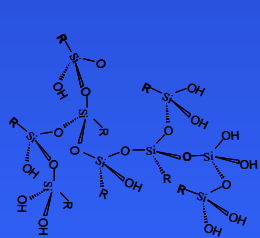
- matériaux inorganiques transparents
- élaborés à basse température
- facilité de mise en forme, notamment en couches minces
- porosité variable : microporeux - mesoporeux

Contrôle de la porosité : les matériaux mésoporeux

assemblages micellaires d'un tensio-actif en solution



mésopore (2-10 nm)

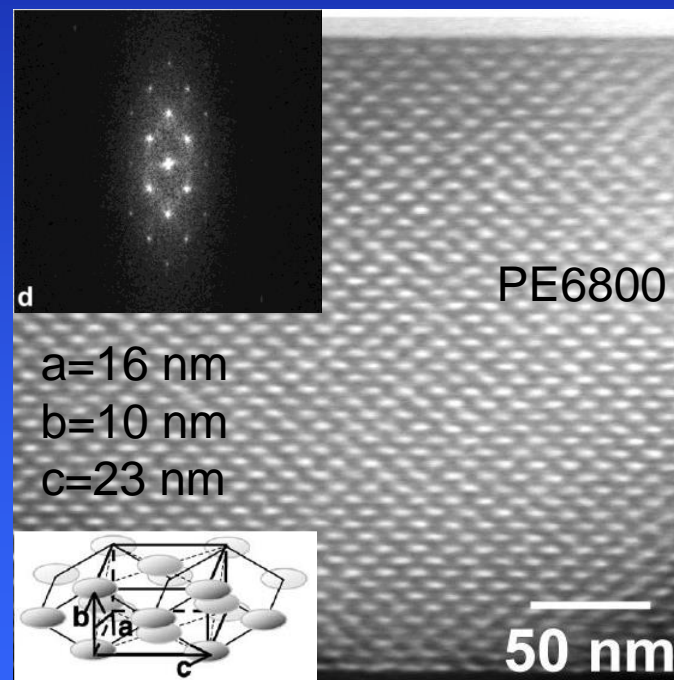
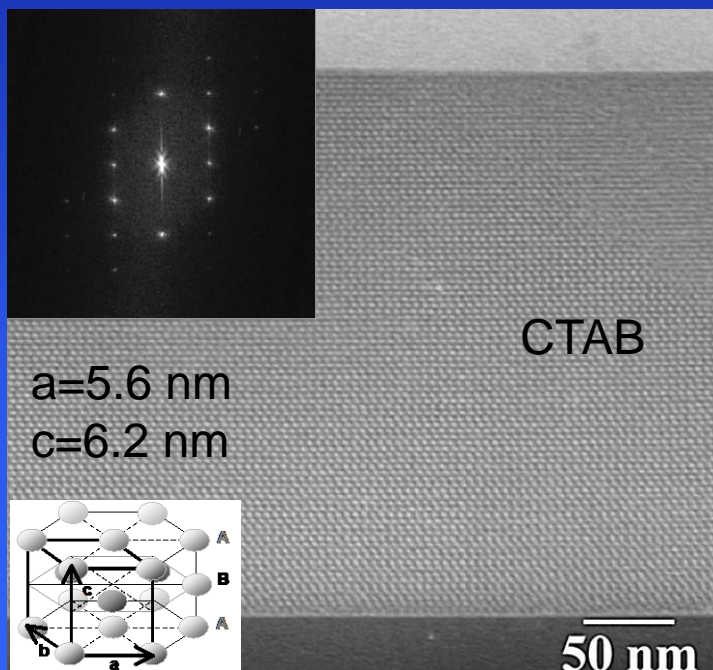
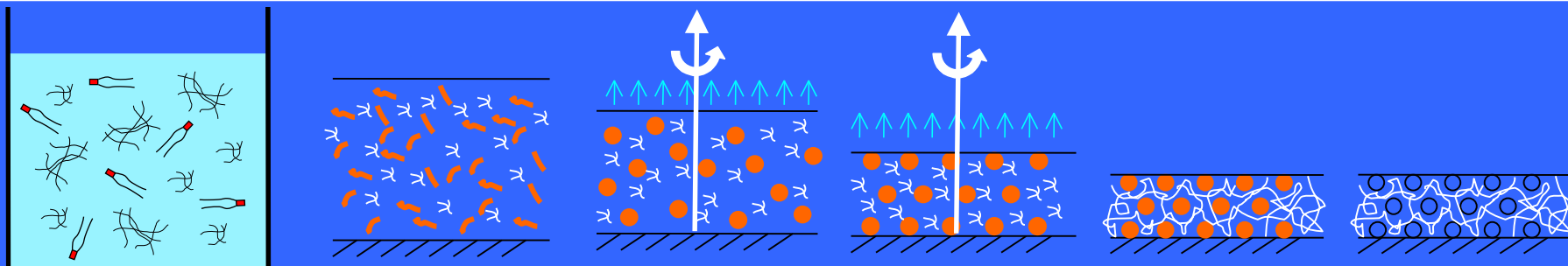


Beck et al, 1992

- littérature (1998): essentiellement des poudres
- Couches minces mésoporeuses?

➔ **Thèse de Sophie Besson**
(Saint-Gobain, C. Jacquiod)

Contrôle de la porosité : matériaux mésoporeux



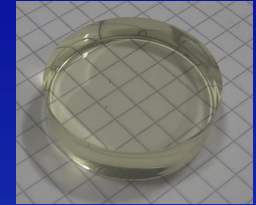
- Films ordonnés sur toute leur épaisseur (300 nm)
- Structure variable (conditions de synthèse, nature du tensio-actif)
- Forte porosité (typ. 25% mesopores, 25% micropores)

La silice sol-gel : pour quoi faire?

Matériau inorganique transparent : matériaux pour l'optique

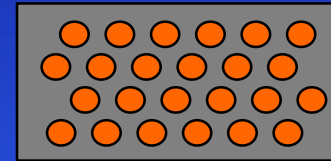
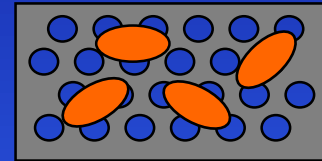
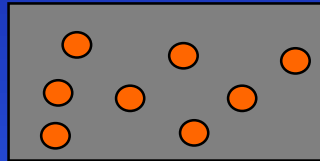
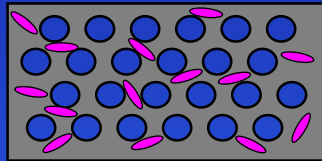
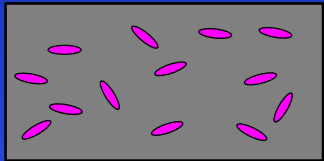
Chimie douce : Incorporation de systèmes optiquement actifs

➔ Matrices sol-gel



 Molécules organiques

 Nanoparticules



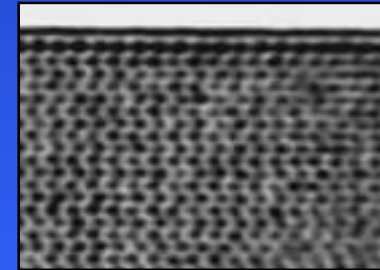
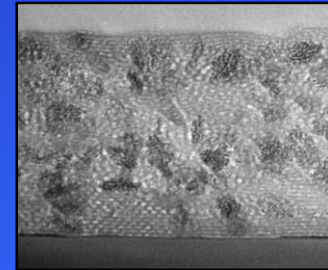
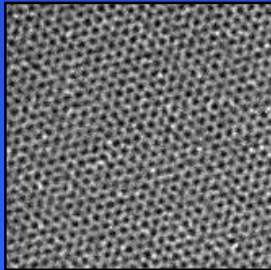
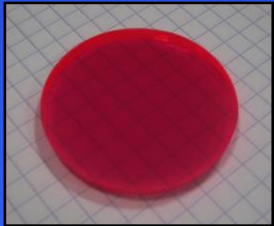
Colorants (F. Chaput)

Si - (CH₃)

CdS

TiO₂

CdS



Films mésoporeux hybrides
Thèse de Muriel Matheron
(Essilor)

Films pour la photocatalyse
Thèse d'Emmanuelle Allain
(Saint-Gobain)

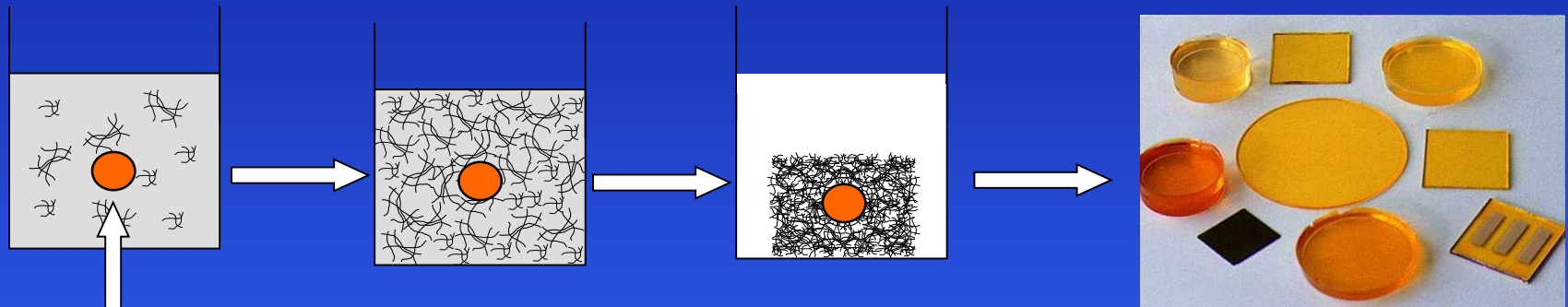
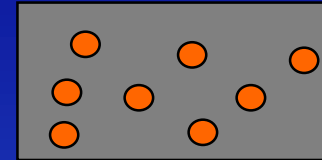
Réseaux 3D de
nanoparticules
thèse de
S. Besson
(Saint-Gobain)

➤ Composites silice / nanoparticules

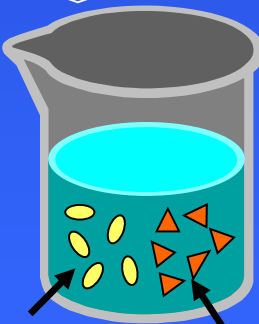
De la chimie sol-gel à la chimie des colloïdes



Effet de confinement quantique (verre $\text{CdS}_{1-x}\text{Se}_x$)

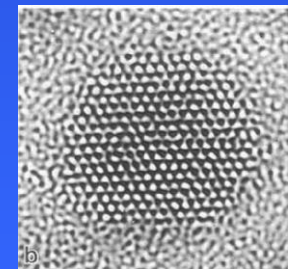
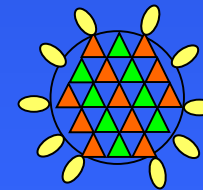


Précurseurs 1

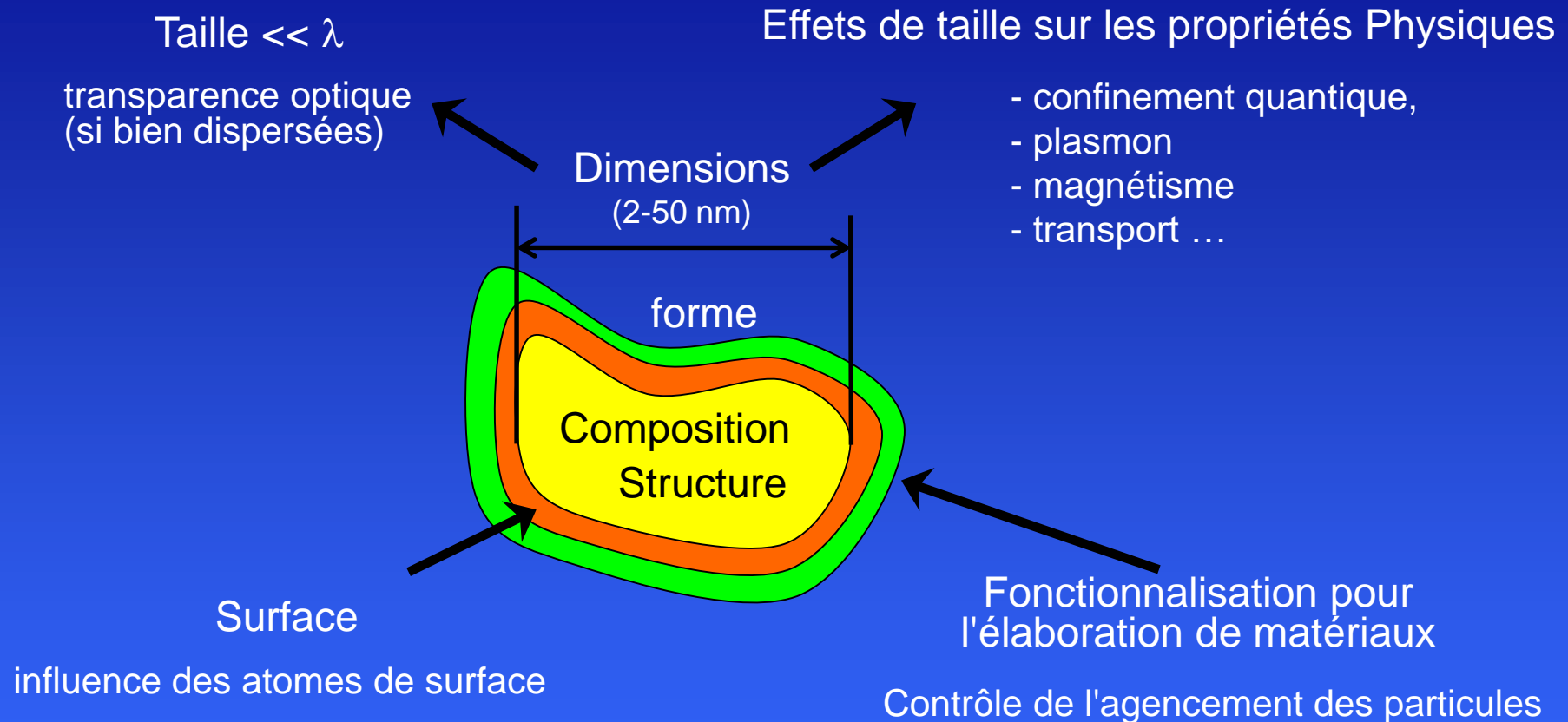


Complexant
organique

Précurseurs 2



Problématiques actuelles de recherche sur les nanoparticules



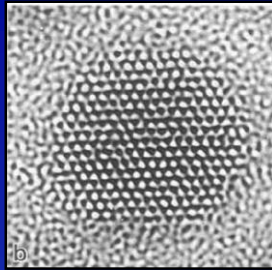
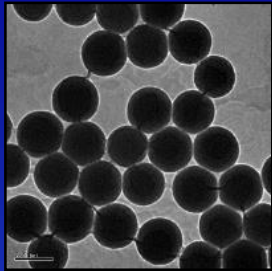
- Contrôle de ces différents paramètres pour l'optimisation d'une propriété
- Maîtrise des distributions

➔ Chimie des colloïdes

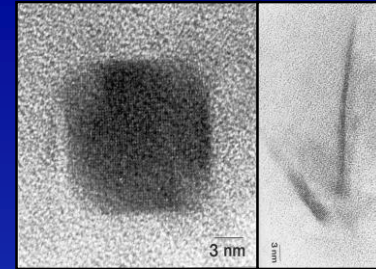
CdS, CdSe, ZnS, **CdS:Mn**

PbS

Silice

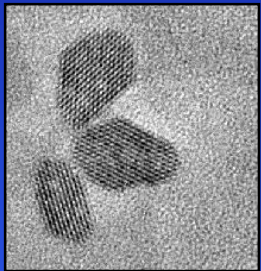


Confinement quantique
luminescence



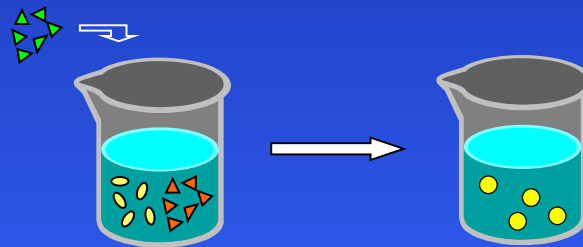
Confinement quantique

TiO₂

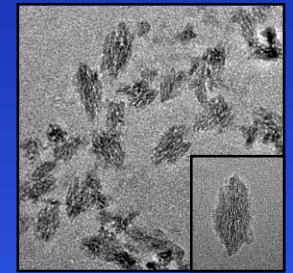


Photocatalyse

I. Synthèse colloïdale de nanoparticules

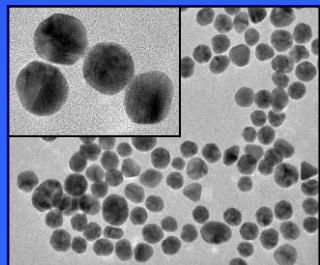


YVO₄:Eu



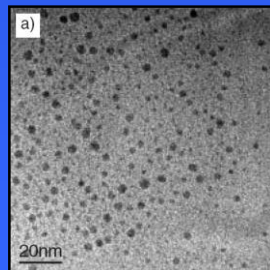
Luminescence

Ag, Au



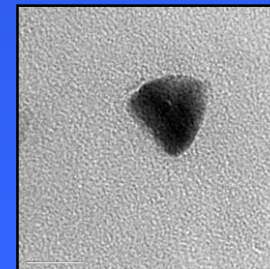
résonance plasmon

Ni[Cr(CN)₆]



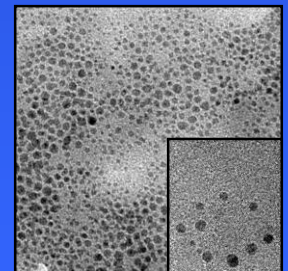
Magnétisme

diamant



Luminescence

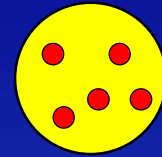
LaPO₄:Ce,Tb



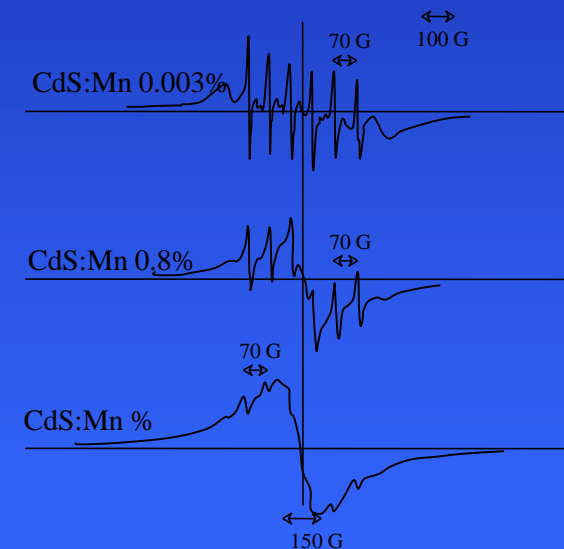
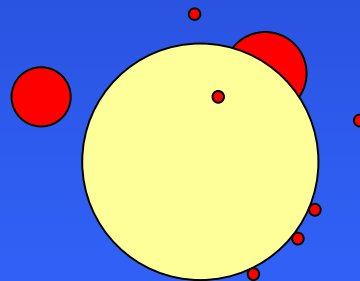
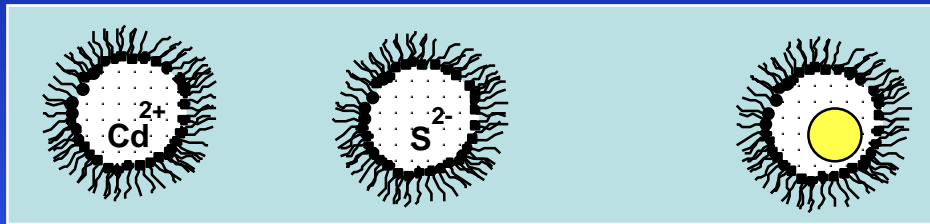
Luminescence

Le problème de l'élaboration de solutions solides Cd_{1-x}Mn_xS

Problématique : élaboration de nanoparticules de CdS:Mn



Contexte : Propriétés magnéto-Optiques des semiconducteurs - semimagnétiques
Dichroïsme circulaire magnétique, Effet Faraday non-linéaire
Collaboration laboratoire d'Optique Quantique (R. Frey)

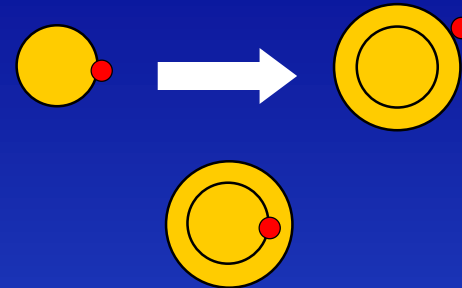


➤ Problème de caractérisation ➡ RPE (Stéphane Esnouf)

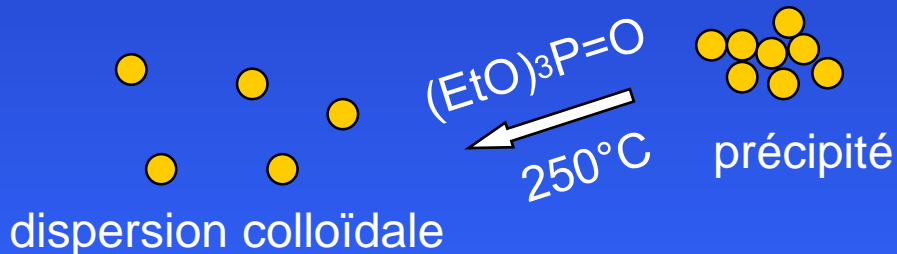
➤ un rendement d'incorporation très faible ➡ **Thèse de Guillaume Counio**

Un problème de cinétique de croissance

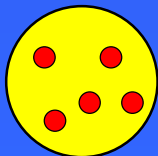
la croissance des nanoparticules en micelles inverses est relativement lente.



➡ il faut la faire plus rapide



➤ rendement d'incorporation amélioré (8% atomique)



➤ Propriétés optiques?

Doping semiconductor nanocrystals

Steven C. Erwin^{1*}, Lijun Zu^{2*}, Michael I. Haftel¹, Alexander L. Efros¹, Thomas A. Kennedy¹ & David J. Norris²

(CdSe / TOPO type Bawendi, voie organométallique)

bulk solubilities of near 50 per cent. These difficulties, which have hindered development of new nanocrystalline materials^{13–15}, are often attributed to 'self-purification', an allegedly intrinsic mechanism whereby impurities are expelled. Here we show instead that the underlying mechanism that controls doping is the initial adsorption of impurities on the nanocrystal surface during growth. We find that adsorption—and therefore doping efficiency—is determined by three main factors: surface morphology, nanocrystal shape, and surfactants in the growth solution. Calcu-

Nature, juillet 2005

Propriétés Optiques : le début des nanoparticules luminescentes à PMC

➤ Propriétés magnéto-Optiques
dichroïsme circulaire magnétique

➤ Luminescence

Giant internal magnetic fields in Mn doped nanocrystal quantum dots

D.M. Hoffman^a, B.K. Meyer^a, A.I. Ekimov^{b,*}, I.A. Merkulov^b, Al.L. Efros^c, M. Rosen^c,
G. Couino^d, T. Gacoin^d, J.P. Boilot^d

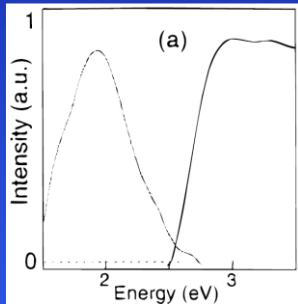
^aPhysikalisches Institut, Justus-Liebig-Universität Giessen, D-35392 Giessen, Germany

^bA.F. Joffe Physical-Technical Institute, 194021 St. Petersburg, Russia

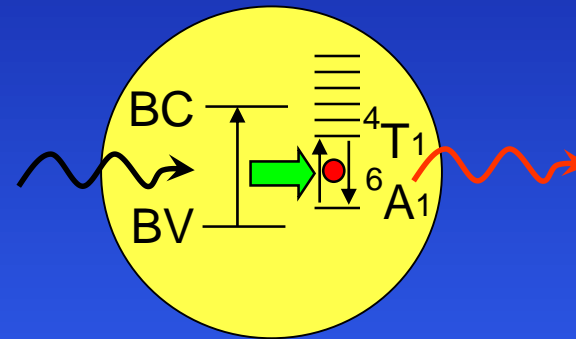
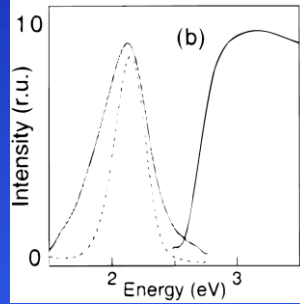
^cNanostructure Optics Section, Naval Research Laboratory, Washington, DC 20375, USA

^dLaboratoire de Physique de la Matière Condensée, École Polytechnique, 91128 Palaiseau, France

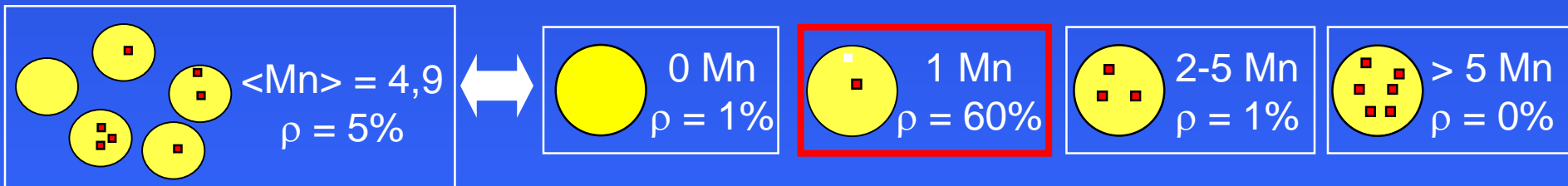
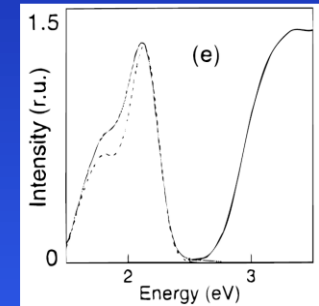
<Mn>=0 ρ = 1%



<Mn>=1 ρ = 20%



<Mn>=4,9 ρ = 5%



- Peu d'ions dopants : distribution de leur nombre par particules
- Le piégeage rapide de l'excitation sur des états localisés permet d'éviter la recombinaison radiative de surface
- Rendements d'émission suffisants pour des applications (idem CdSe/ZnS)

Nanoparticules Luminescentes : Des sulfures aux oxydes

Nanoparticules luminescentes : pour quelles applications?

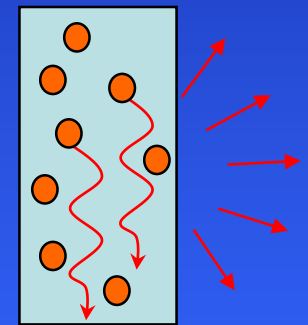
- Les mêmes que les colorants fluorescents, la photostabilité en plus
- Les mêmes que les poudres luminophores inorganiques, la transparence en plus

⇒ marqueurs, sondes, pigments, affichage, optique intégrée ...

Objectif :

- élaboration par voie colloïdale de nanoparticules fortement luminescentes
- incorporation en matrices sol-gel

Excitation

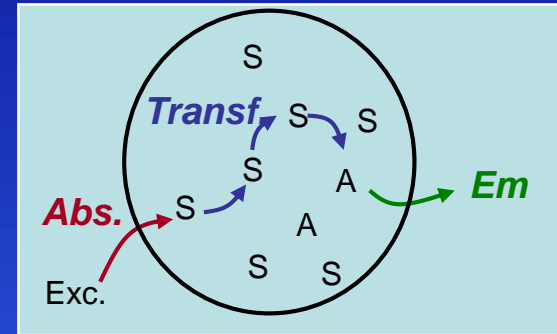
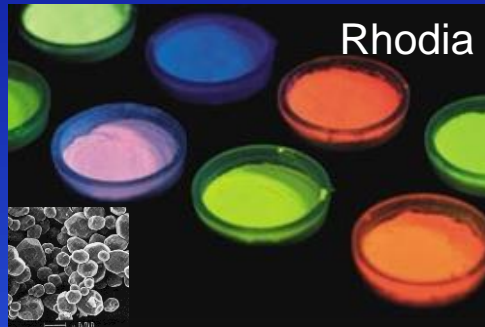
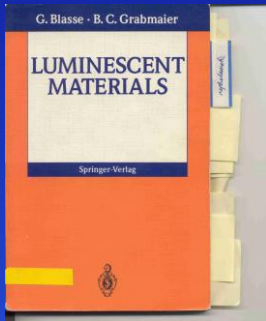


emission

➤ **Thèse d'Arnaud Huignard**
(financement DGA)

Le choix du système

- 1) les composés intéressants à faire sous forme de nanoparticules sont principalement ceux qui possèdent déjà des propriétés intéressantes à l'état massif



halogénures : BaF_2 : Eu, Ce ...

chalogénures : ZnS:Mn , ZnS:Ag,Cl

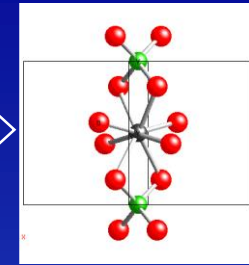
Oxydes : PbWO_4 , $\text{Y}_2\text{O}_3\text{S:Eu}$, $\text{LaPO}_4\text{:Ce,Tb}$, $\text{BaMgAl}_{10}\text{O}_{17}\text{:Eu}$...

2) Pas les chalcogénures

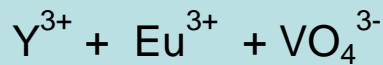
3) Synthèse colloïdale envisageable, une condition essentielle :
Solide pouvant être obtenu à l'état crystallisé par réaction de précipitation à partir de précurseurs dissous en solution

➤ YVO_4 dopé terres rares

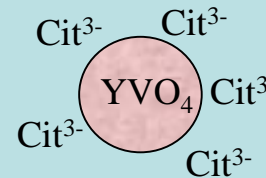
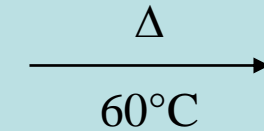
Nanoparticules de vanadate d'Yttrium



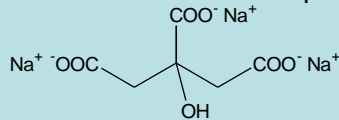
YVO₄
cristallisé
(zircon)



Nono 1 (40 nm)



Nono 2 (7 nm)



400 g/l

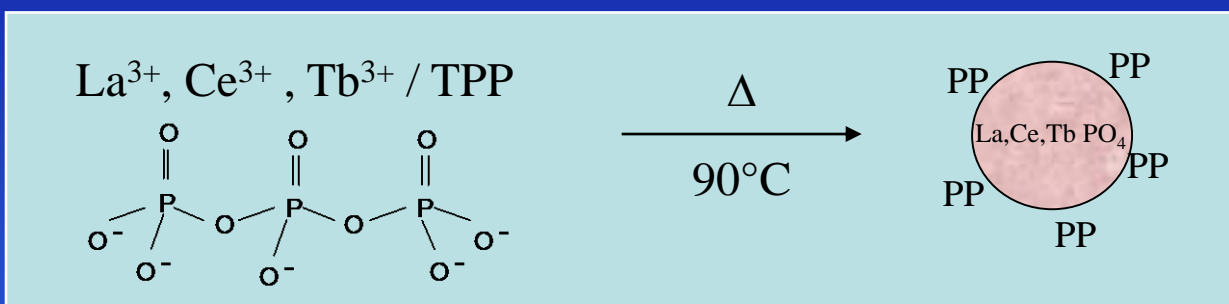


- Solution solide Y_{1-x}Eu_xVO₄ possible entre 0 et 1,
- Rendements quantique 10-20% (CdSe/ZnS dans l'eau : 18%)
- Synthèse "simple et efficace" dans l'eau
- **Thèse de Valérie Buissette (Rhodia)**

Nanoparticules de LaPO₄

- Objectif de la thèse de Valérie Buissette : matériaux émettant dans le blanc
- Blanc = rouge + vert + bleu

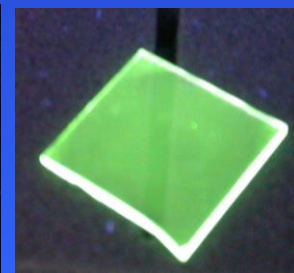
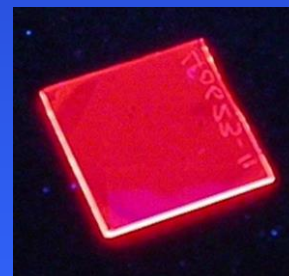
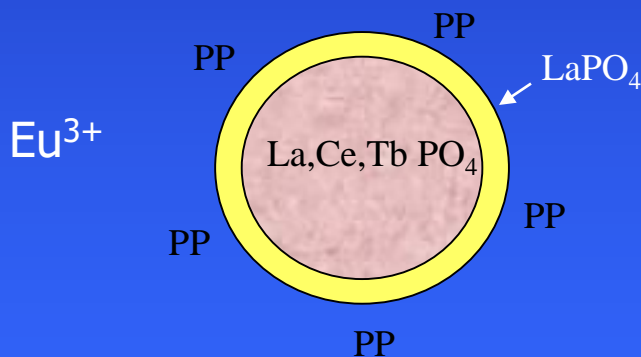
Luminophore vert massif : LaPO₄:Ce,Tb



Q (Tb³⁺) = 45 %

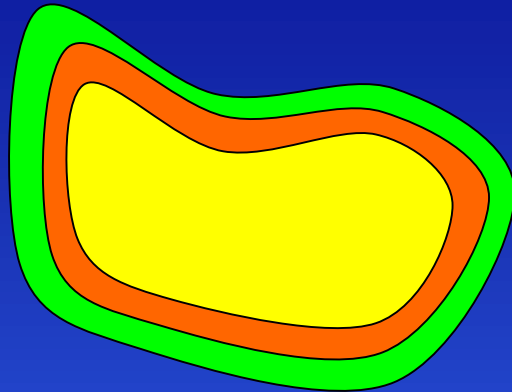


Ce³⁺, Tb³⁺



- Synthèse originale de nanoparticules de phosphates
- Décalage de la raie d'émission du cérium dans le visible : émission UV - bleu
- Stabilisation du Ce³⁺ par élaboration de structures cœur/coquille
- Elaboration de matériaux transparents luminescents (couches minces)

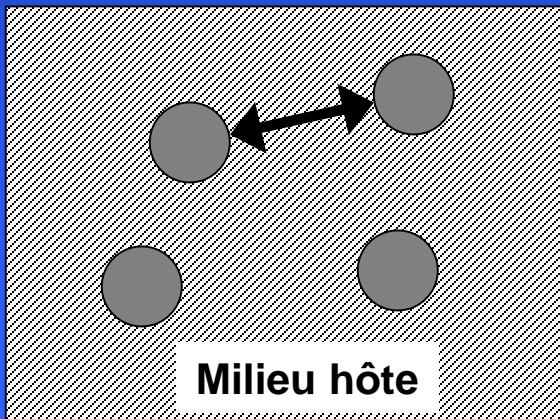
Des nanoparticules aux matériaux : fonctionnalisation



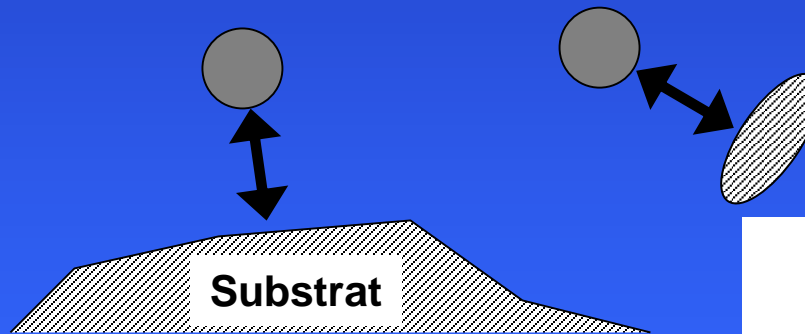
Fonctionnalisation pour l'élaboration de matériaux



Contrôle de l'agencement des particules



Milieu hôte

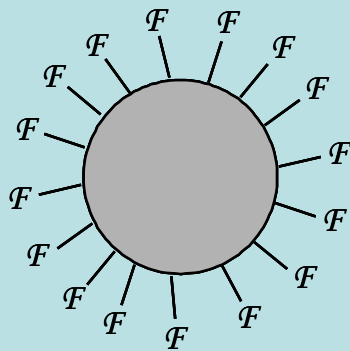
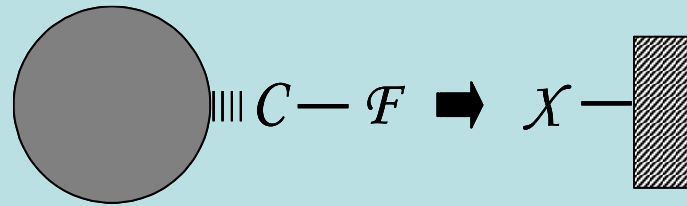


Substrat

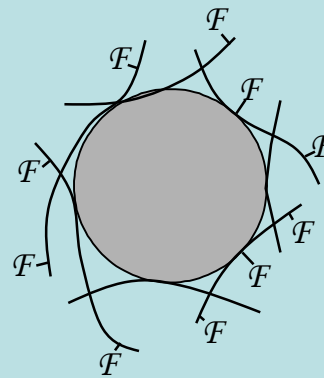
Molécule,
nanoparticule,
système biologique

➤ Fonctionnalisation = greffage de fonctions chimiques en surface des particules

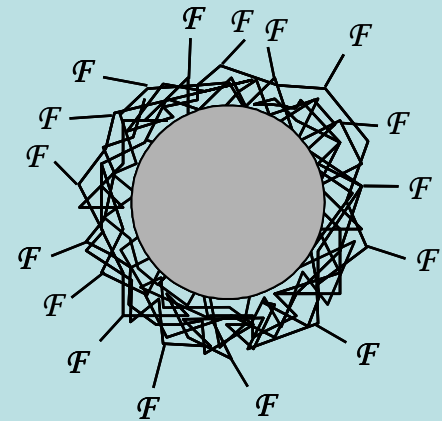
Stratégies de fonctionnalisation des nanoparticules



greffage direct



polymères



encapsulation

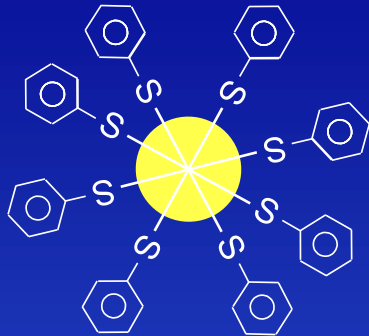
2 exemples :

Gels de CdS

sondes biologiques

Fonctionnalisation de nanoparticules de CdS

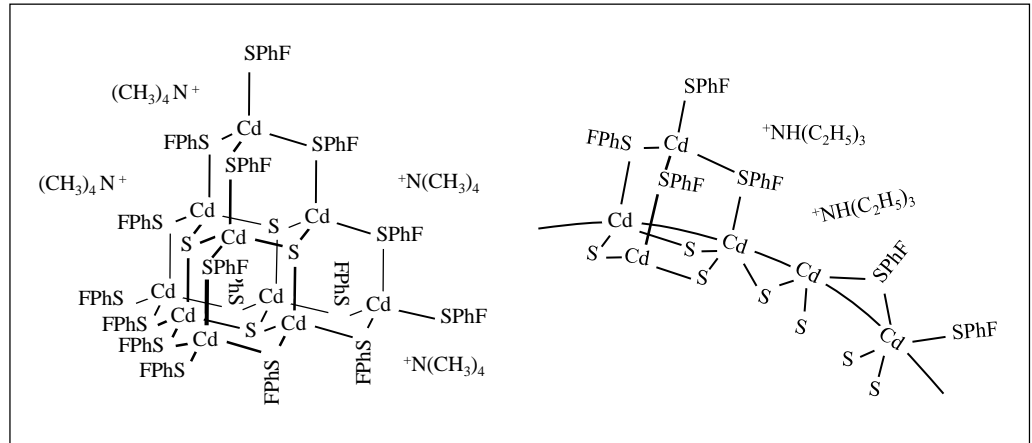
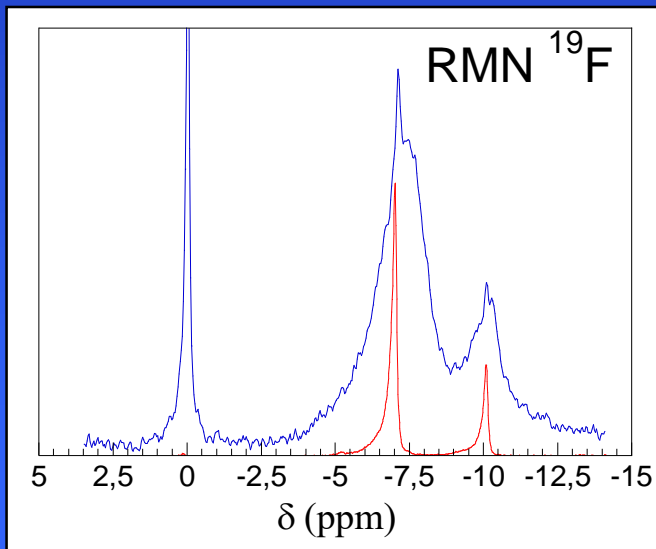
Nanoparticules de CdS complexées par le phénylthiol



solutions très concentrées dans la pyridine

Quelle est la structure de surface du complexe?

Étude par RMN (L. Malier) : ^{113}Cd , H, C mais faible sensibilité $-\text{SPh} \rightleftharpoons -\text{SPh-F}$

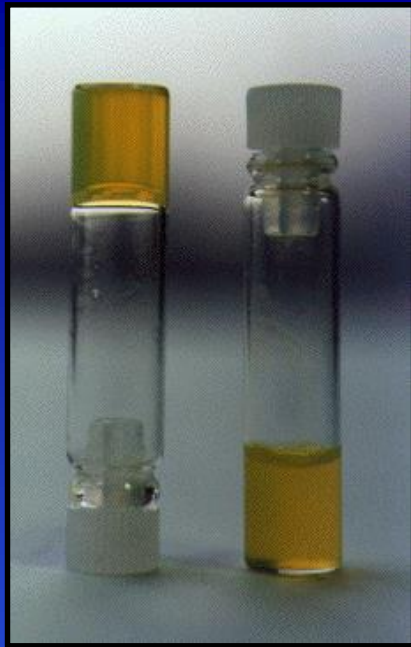


Clusters de Dance

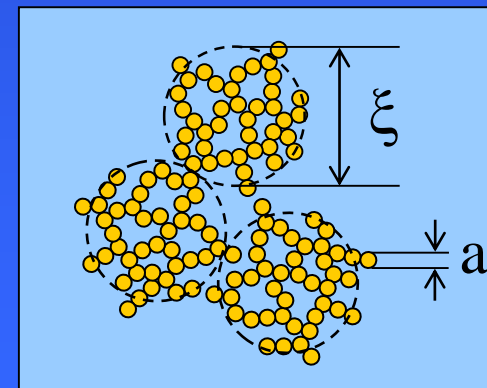
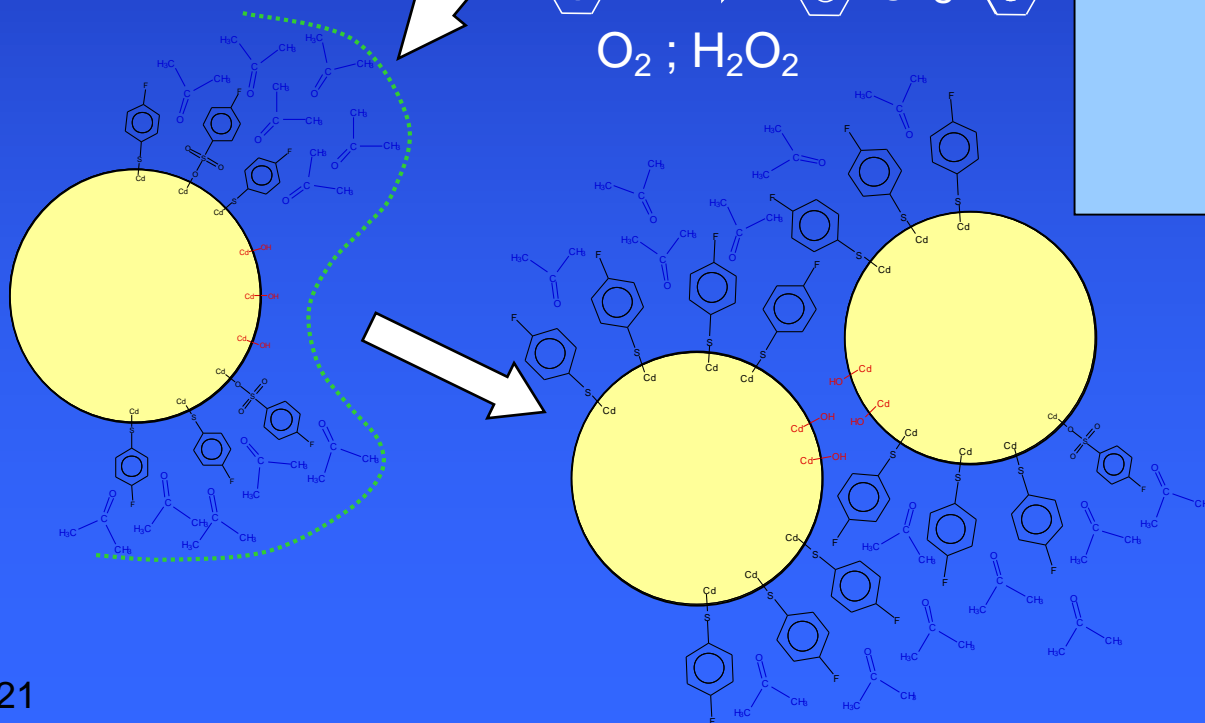
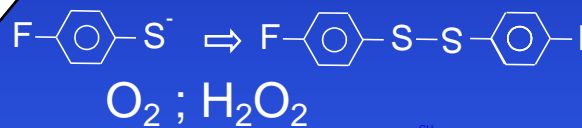
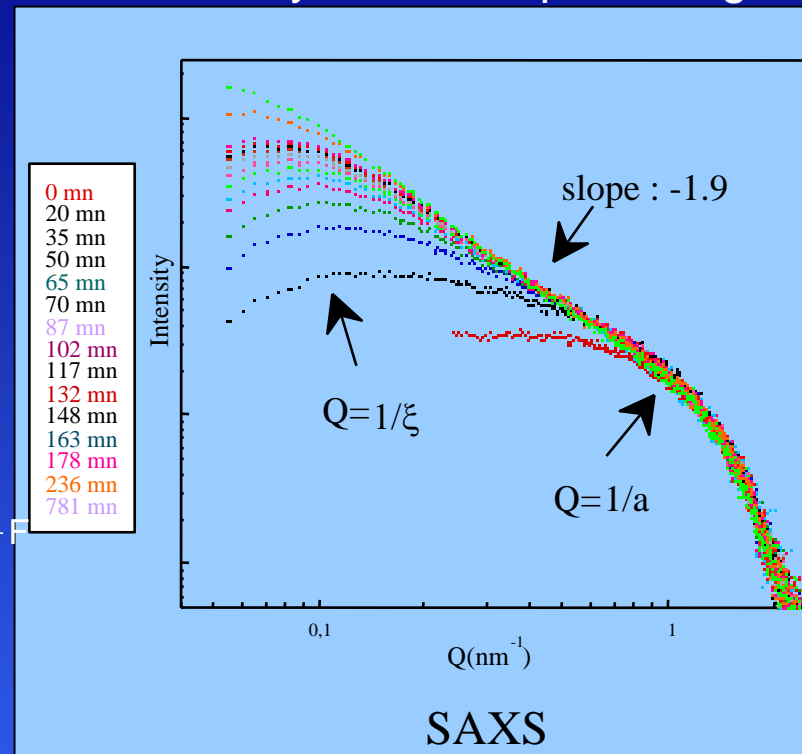
peu stable dans la pyridine

Dispersion extraordinaire dans l'acétone !

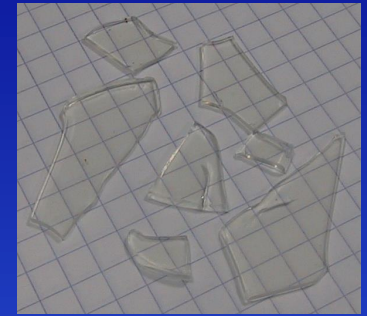
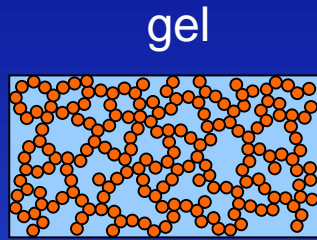
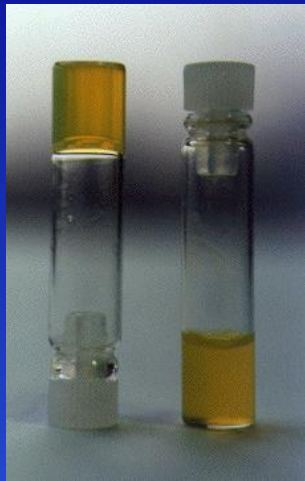
Gels de CdS



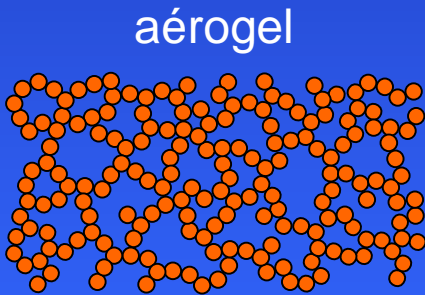
diffusion des rayons X aux petits angles



Vers une application du procédé sol-gel aux chalcogénures



xérogel de silice



Sol-gel Processing of Semiconducting Metal Chalcogenide Xerogels

*Indika U. Arachchige, Jaya L. Mohanan, Stephanie L. Brock**

Department of Chemistry, Wayne State University, Detroit, MI 48202, USA.

Chemistry of Materials (soumis en juin 2005)

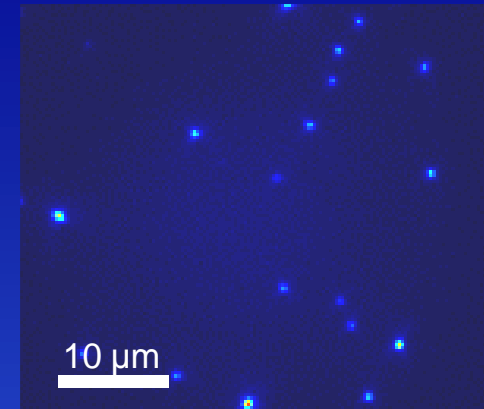
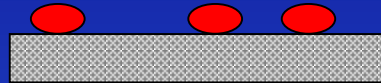
Porous Semiconductor Chalcogenide Aerogels

Jaya L. Mohanan, Indika U. Arachchige, Stephanie L. Brock*

SCIENCE VOL 307 21 JANUARY 2005

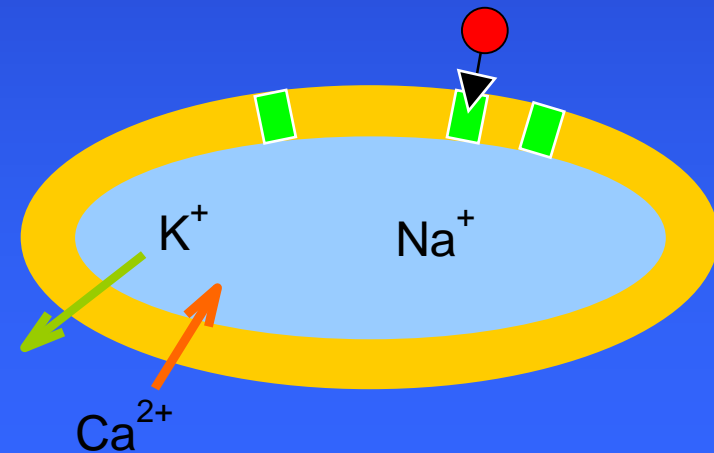
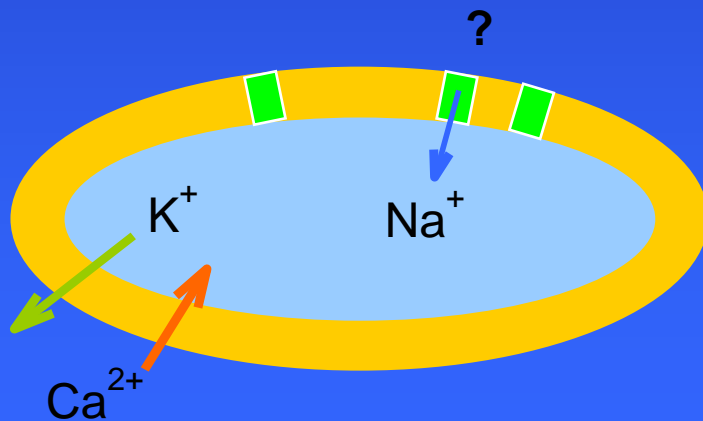
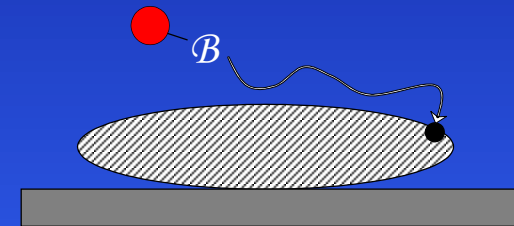


Les nanoparticules luminescentes comme sondes pour la biologie



➤ Application comme sondes pour la biologie ?

E. Beaufrepaire, M-P. Sauviat, A. Alexandrou
Laboratoire d'Optique et Biosciences, Ecole Polytechnique



➤ **Thèse de Domitille Giaume (Didier Casanova, LOB)**

Fonctionnalisation des particules

Saxitoxin STX

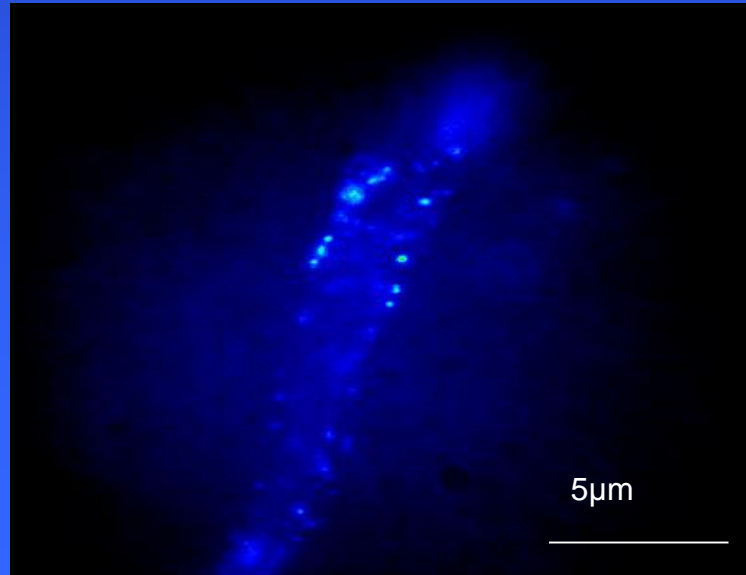
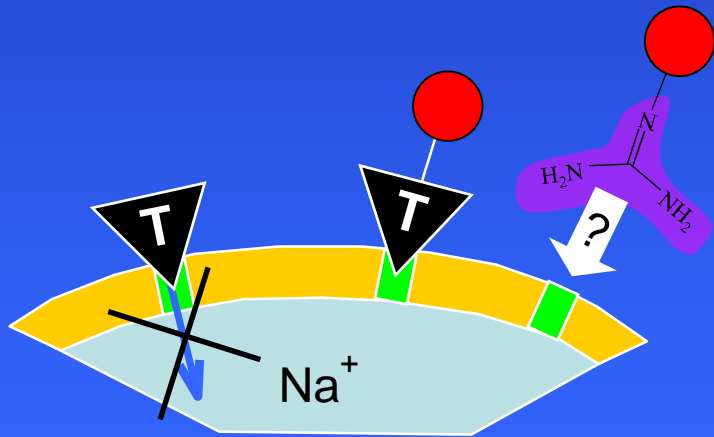
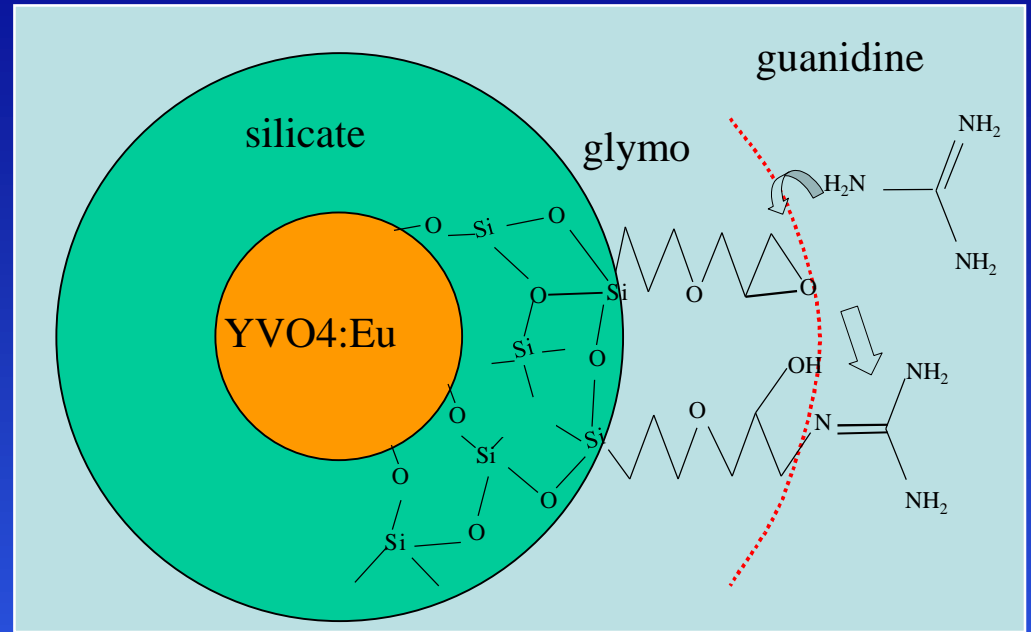
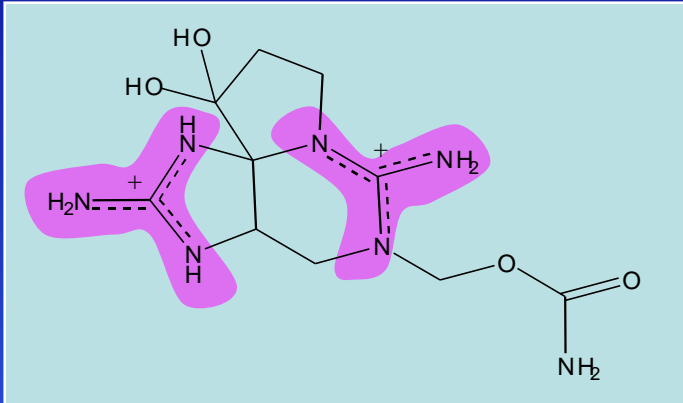


Image de
microscopie
de
fluorescence

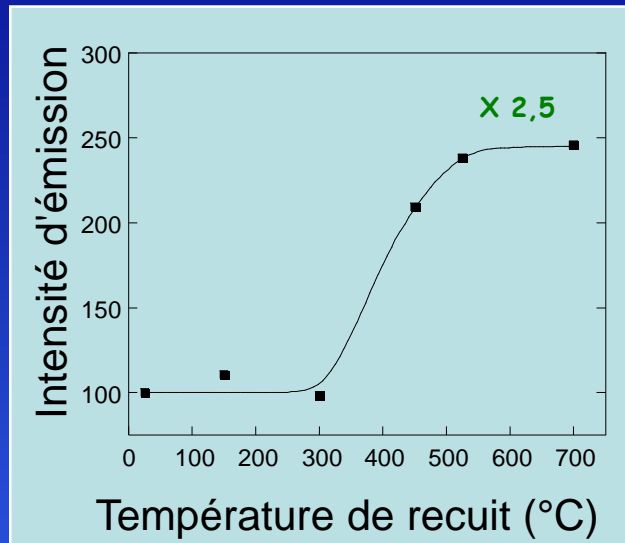
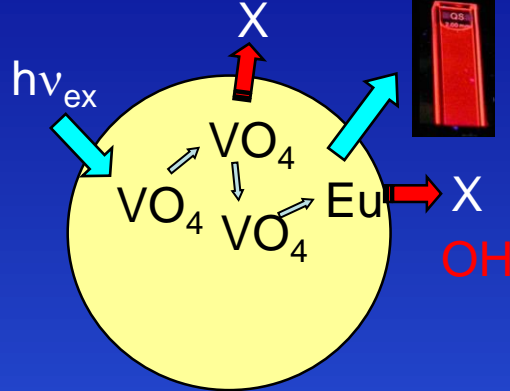
Laboratoire
d'Optique et
Bioscience

D. Casanova

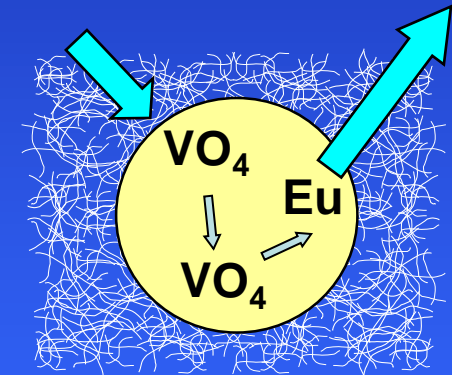
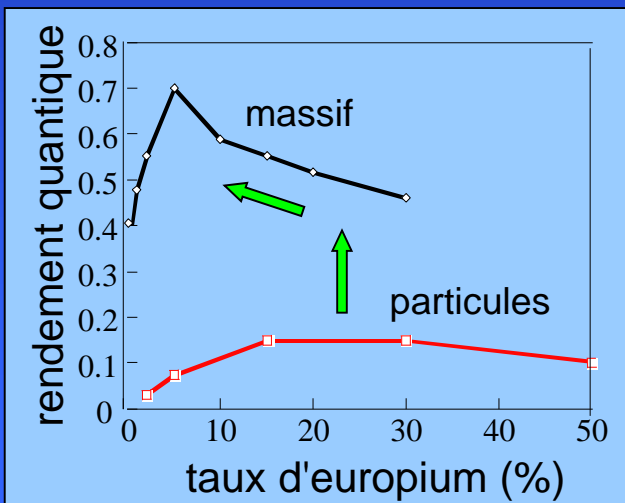
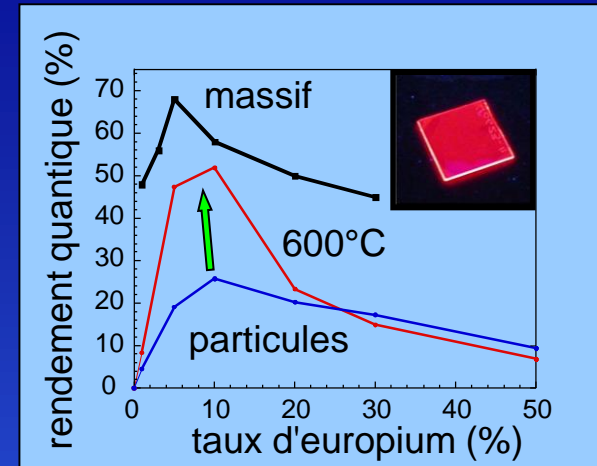
Projets

Amélioration du rendement quantique de nanoparticules d'oxyde dopées terres rares

$\rho = 10-20\%$



thèses V. Buissette, A. Huignard

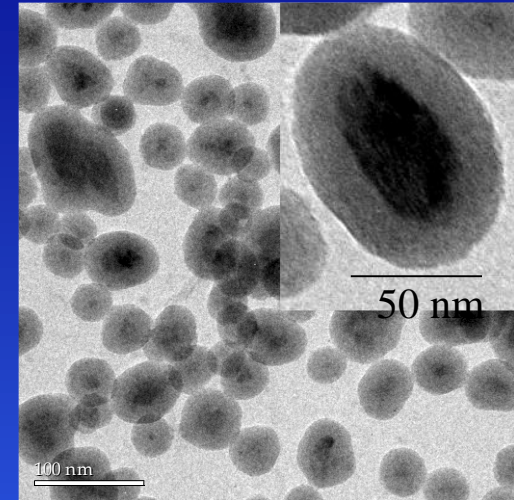
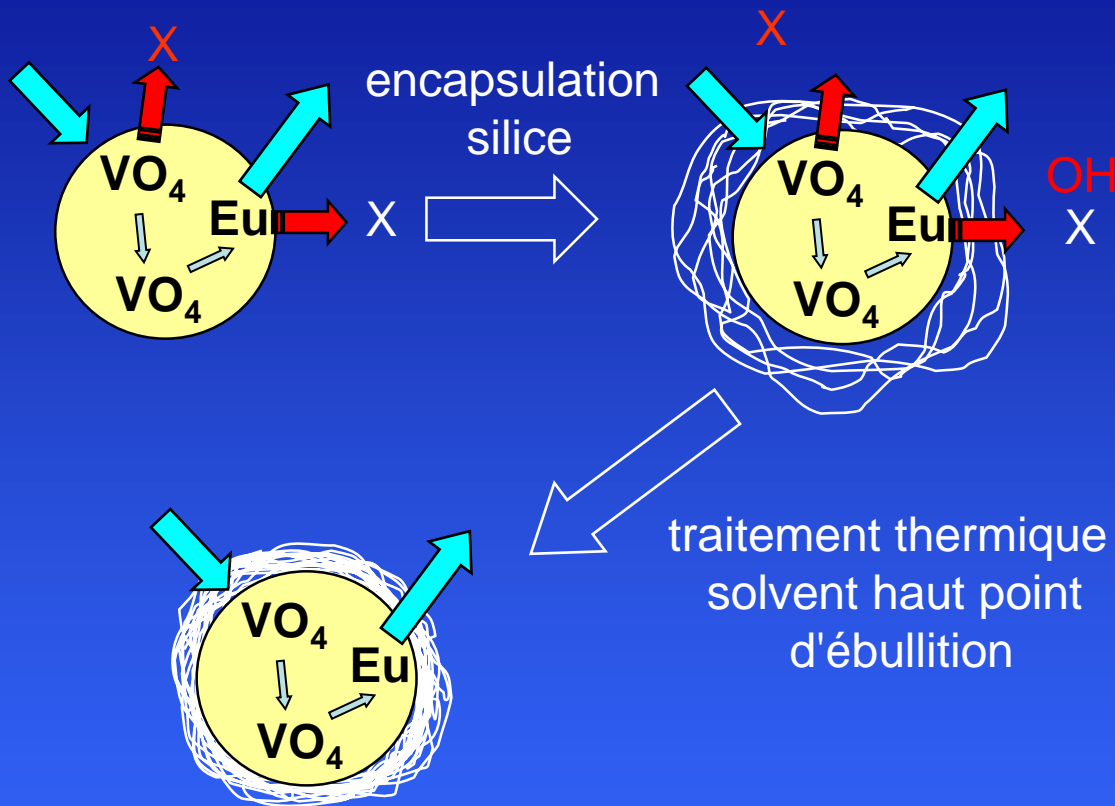


traitement thermique : condensation de la silice, déshydratation

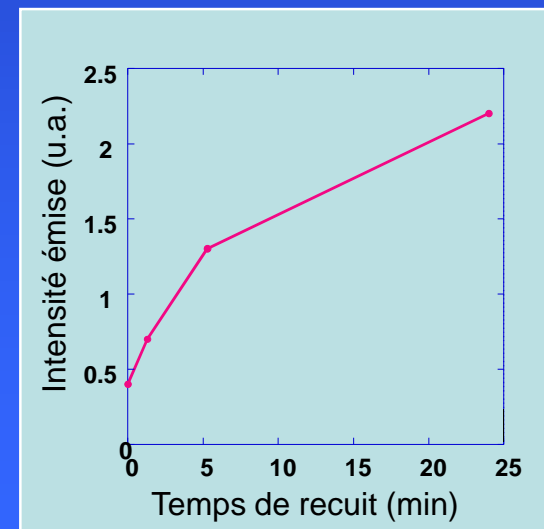
➡ élimination des pièges

➤ peut-on faire la même chose en préservant l'état colloïdal?

Traitement thermique de particules encapsulées



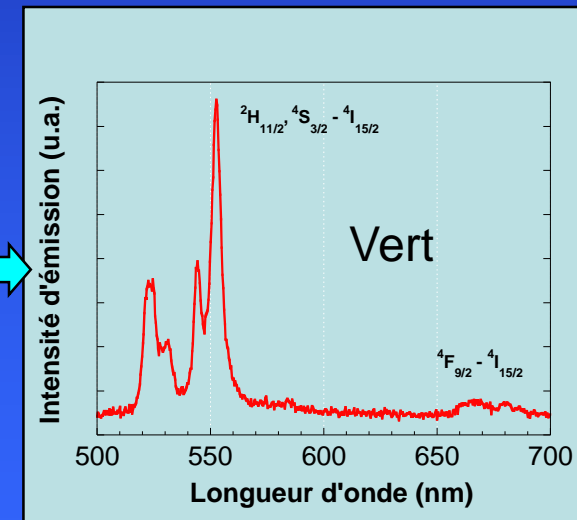
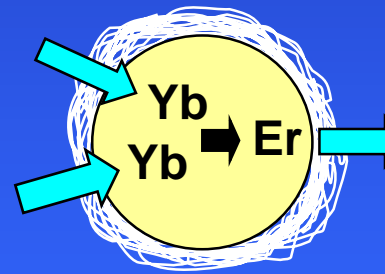
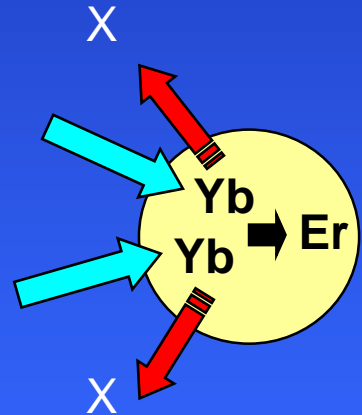
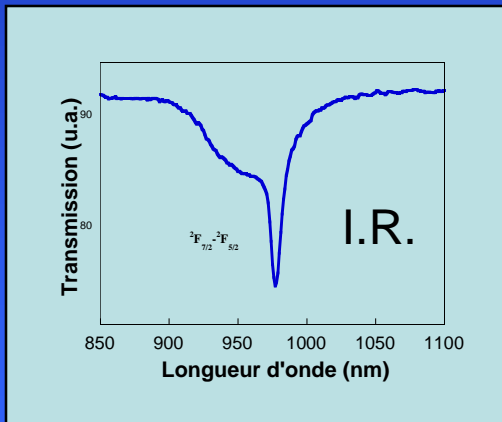
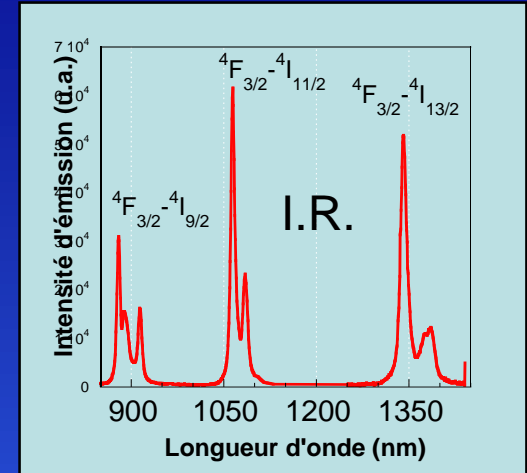
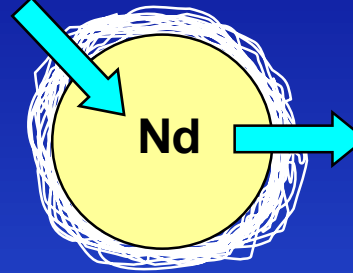
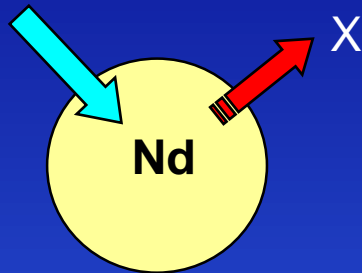
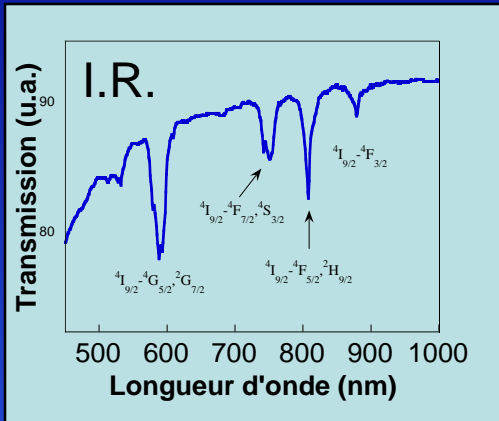
D. Giaume



- résultat à confirmer, agrégation à contrôler
- l'enjeu : émission dans l'infra-rouge

Application aux ions émetteurs dans l'infra-rouge

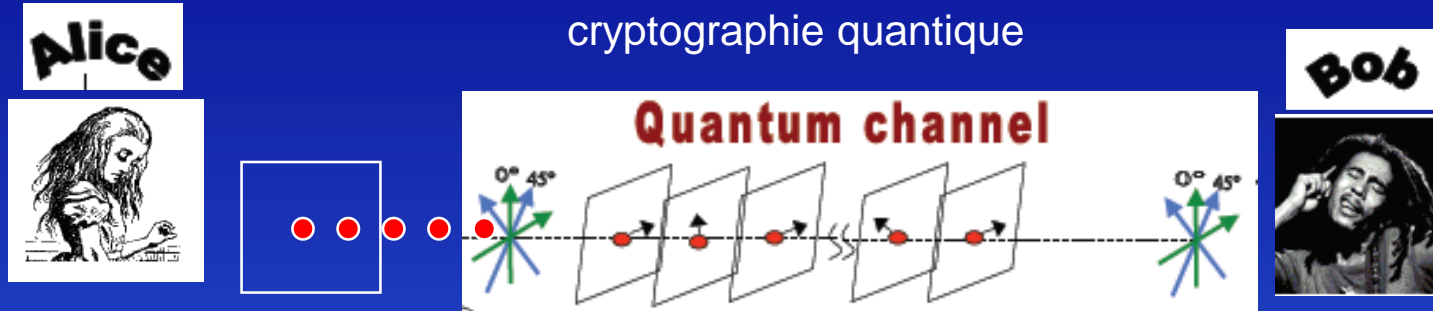
Nd, Er, Yb : très sensibles aux OH \Rightarrow rendements faibles



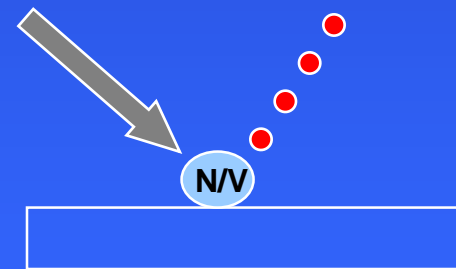
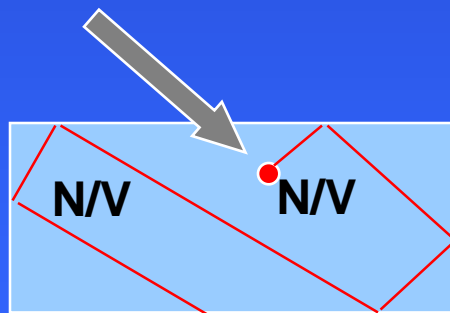
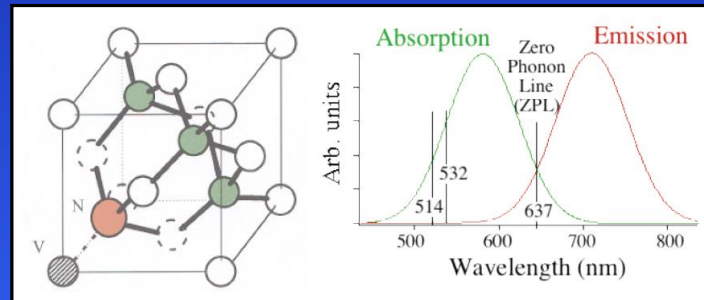
- émission infra-rouge ou "up-conversion" dans le visible
- applications en biologie, matériaux amplificateurs (Er) ...

Nanoparticules de diamant

A. Beveratos, R. Brouri, A. Villing, J-P. Poizat, P. Grangier, Institut d'Optique



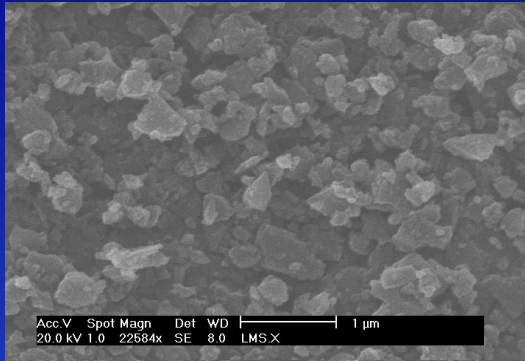
centres N/V du diamant :
rendements élevés
temps de vie ns,
stabilité



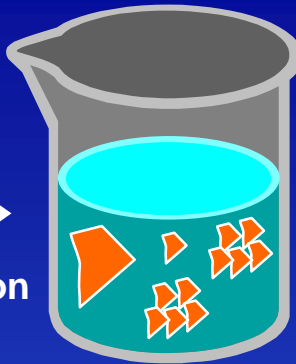
➤ l'indice élevé du diamant empêche l'extraction des photons

➔ nanoparticules $d \ll \lambda$?

Poudre de diamant De Beers, type IIB



sonification



centrifugation sélective



taille :
80 nm



image
topographique
20 μ m x 20 μ m

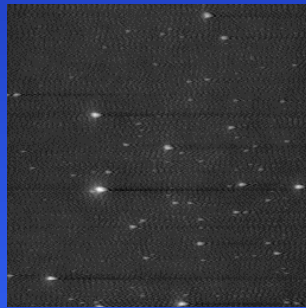
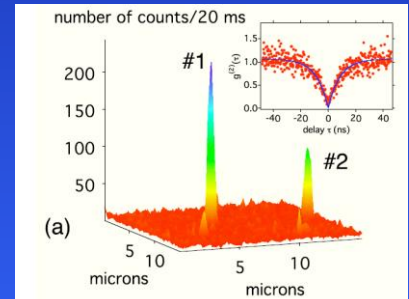
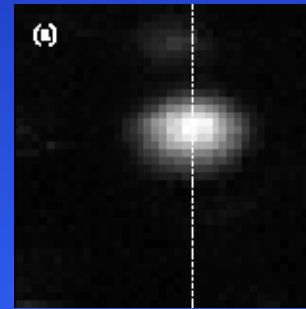


image
optique
(confocal)
2 μ m x 2 μ m



VOLUME 89, NUMBER 18

PHYSICAL REVIEW LETTERS

28 OCTOBER 2002

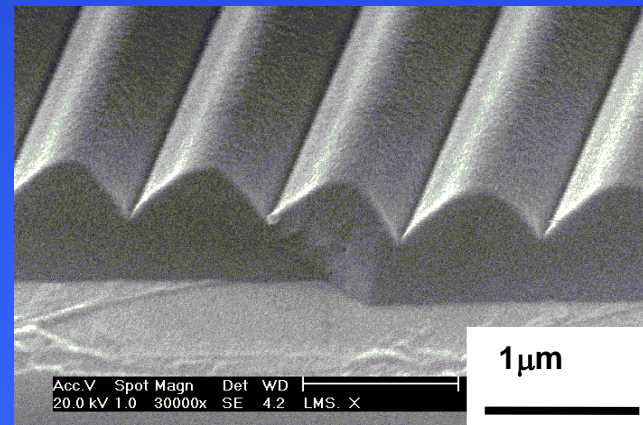
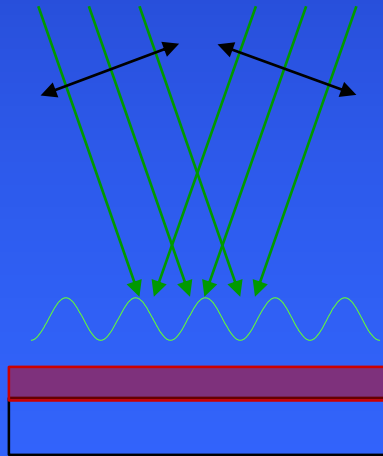
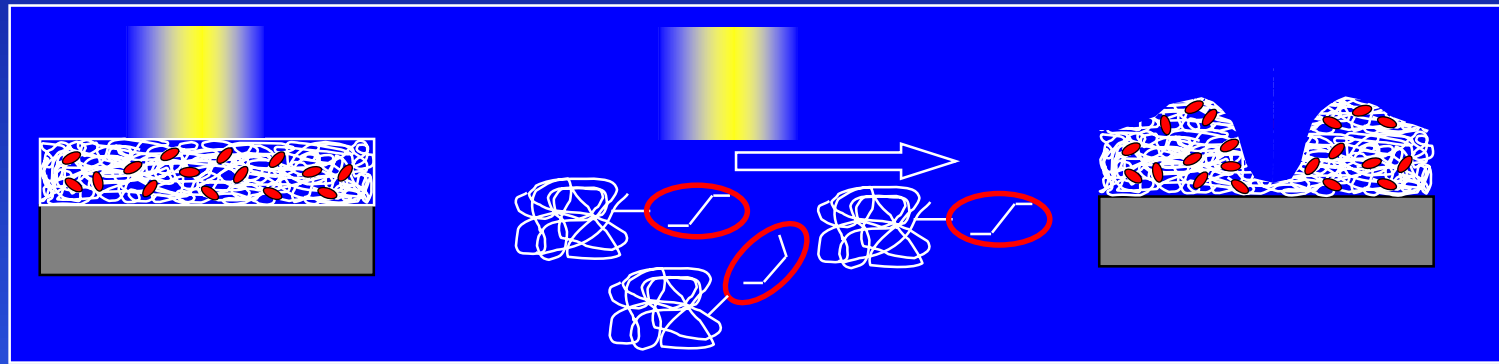
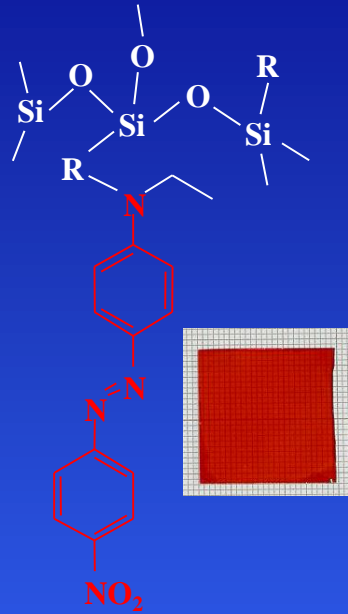
Single Photon Quantum Cryptography

Alexios Beveratos,* Rosa Brouri, Thierry Gacoin,† André Villing, Jean-Philippe Poizat, and Philippe Grangier
Laboratoire Charles Fabry de l'Institut d'Optique, UMR 8501 du CNRS, F-91403 Orsay, France
(Received 6 June 2002; published 10 October 2002)

➤ On peut faire de la physique sur des nanoparticules non accessibles par voies chimiques (si il n'en faut pas beaucoup).

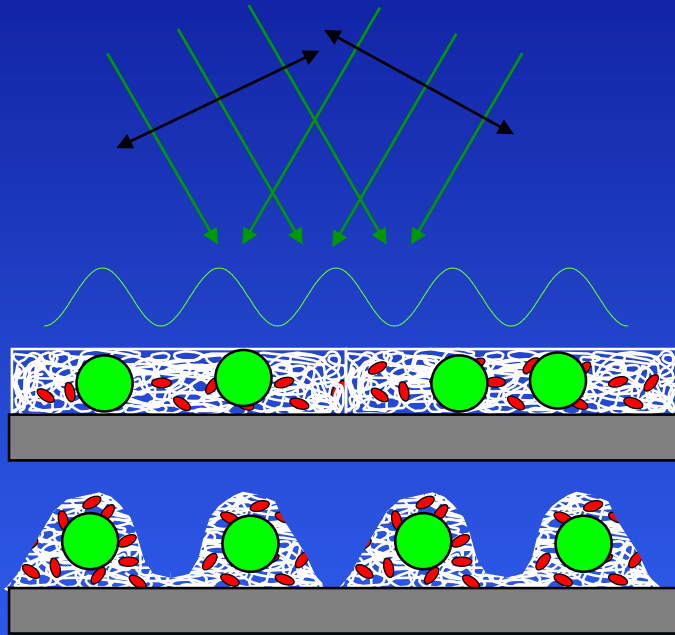
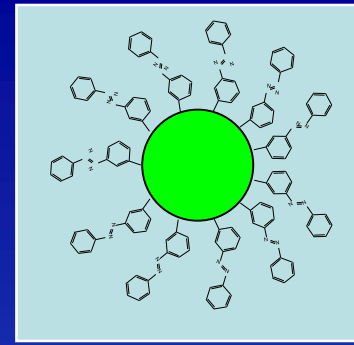
Matériaux photodéformables à base d'azobenzènes (DR1)

Damien Garrot, J. Peretti, Y. Lassailly, K. Lahlil, J-P. Boilot (Groupes EPS et Chimie, labo PMC)



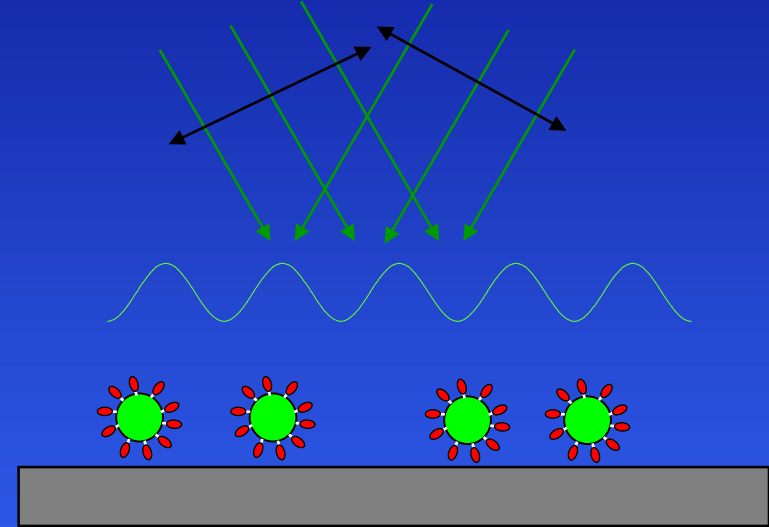
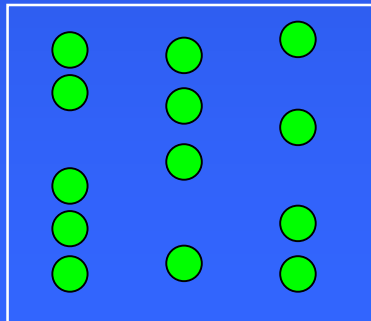
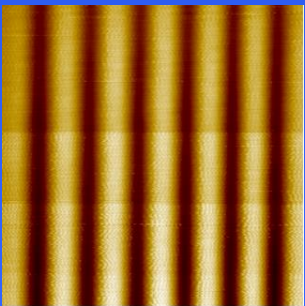
➤ Peut-on déplacer des nanoparticules avec de la lumière?

la première étape : réseaux de nanoparticules ?

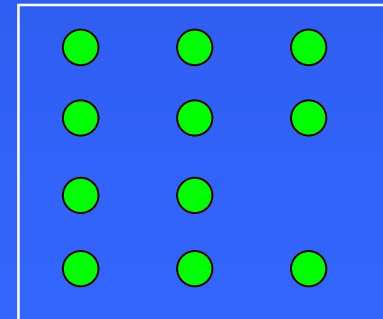
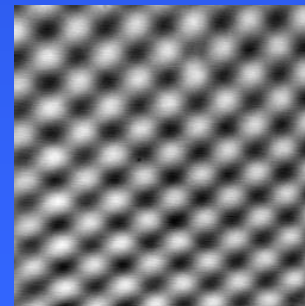


1 x 2 faisceaux

5 μm X 5 μm



2 x 2 faisceaux

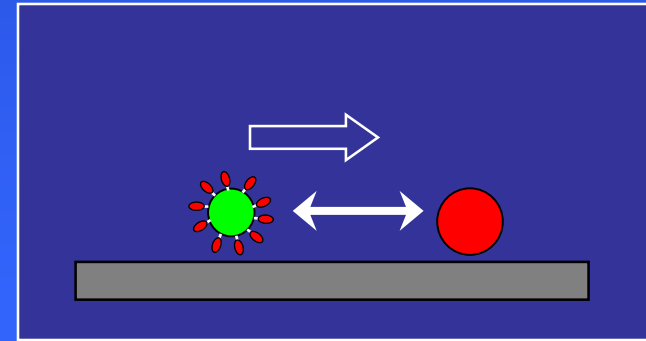
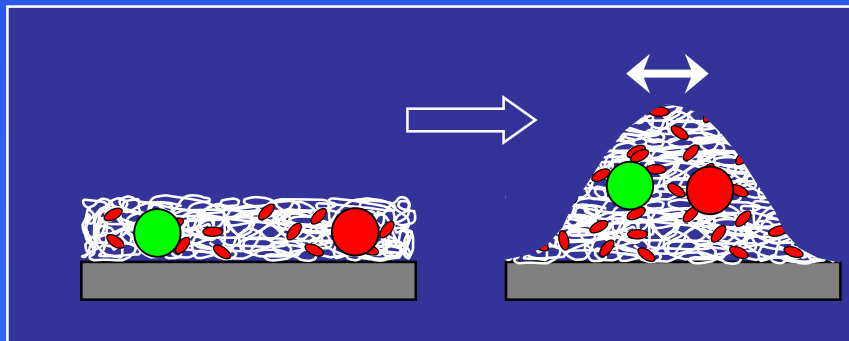
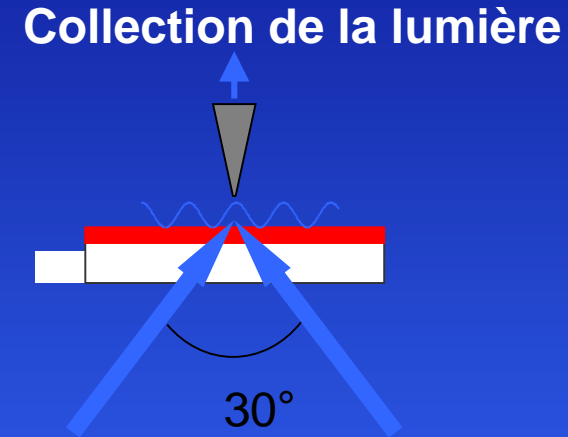
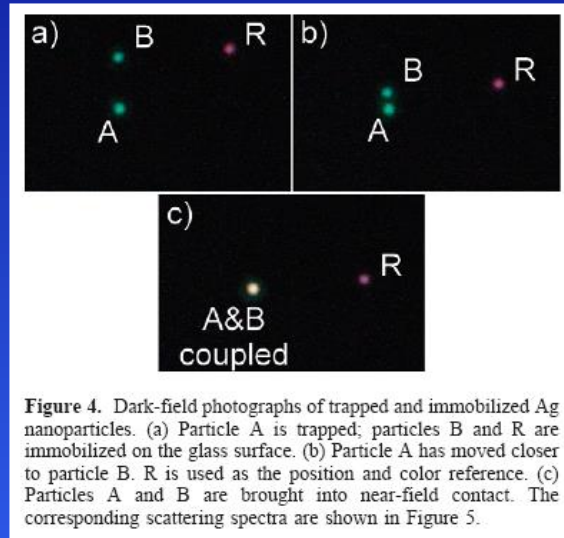


Etude du couplage entre particules

Mise en évidence du couplage entre 2 particules d'argent, manipulées par pinces optiques
Dag Hanstorp, Götteborg, Suède



- transferts d'énergie (luminescence)
- couplage plasmon (absorption)
- exaltation plasmon (luminescence)
- magnétisme (magnéto-optique)





Guillaume Counio



Arnaud Huignard



Sophie Besson



Valérie Buisette



Mélanie Moreau



JPB

Khalid Lahlil



Emmanuelle Allain



Caroline Bertail-Huré



Domitille Giaume

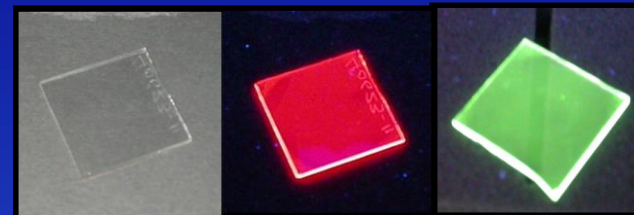
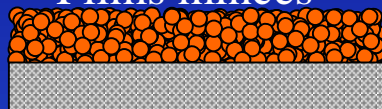


Muriel Matheron

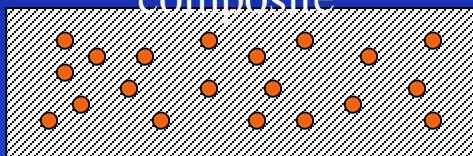
Matériaux à base de nanoparticules



Films minces



composite



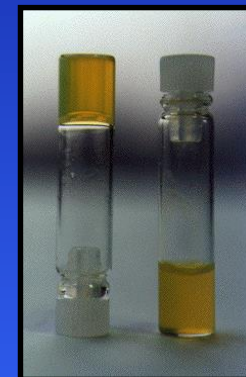
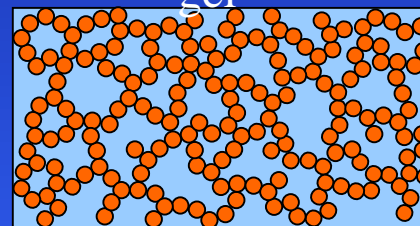
Réseau 2D



Particule unique



gel



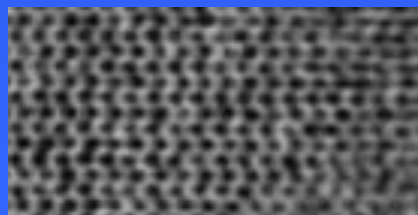
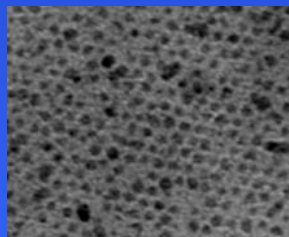
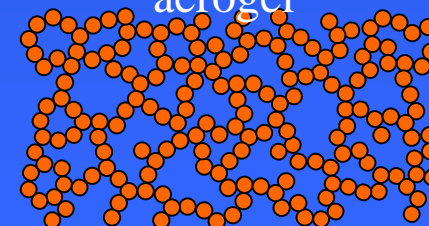
Réseau 3D



xerogel

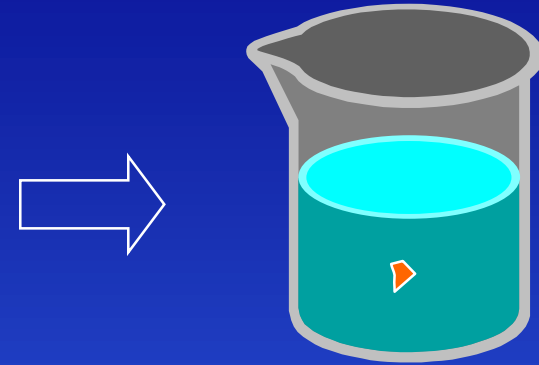
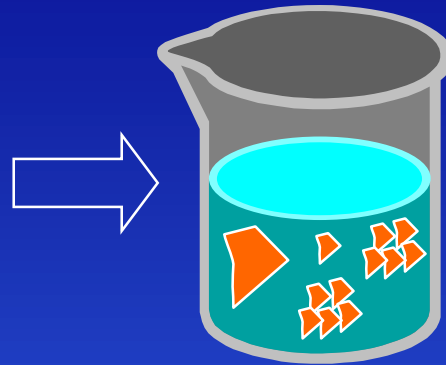
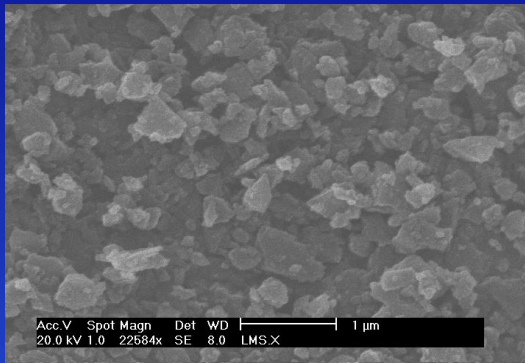


aerogel

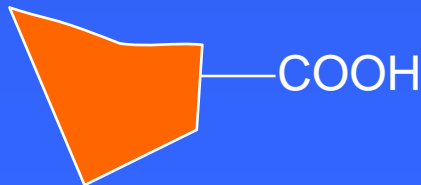
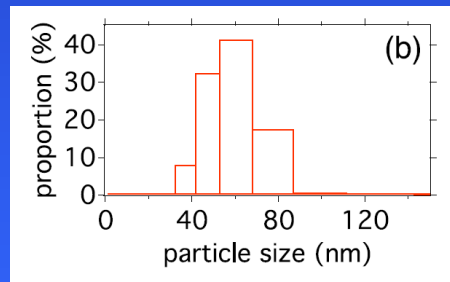
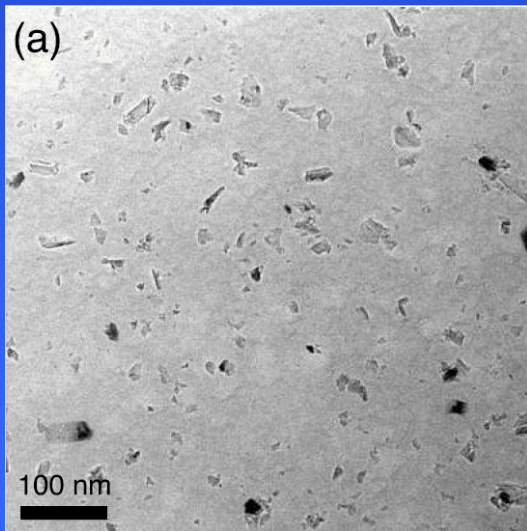


Autres applications?

F. Treussard, J-F. Roch



Diamant de détonation (Van Moppes)



Photoluminescence of single colour defects
in 50 nm diamond nanocrystals

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