Assemblages de supercristaux par approche prédictive

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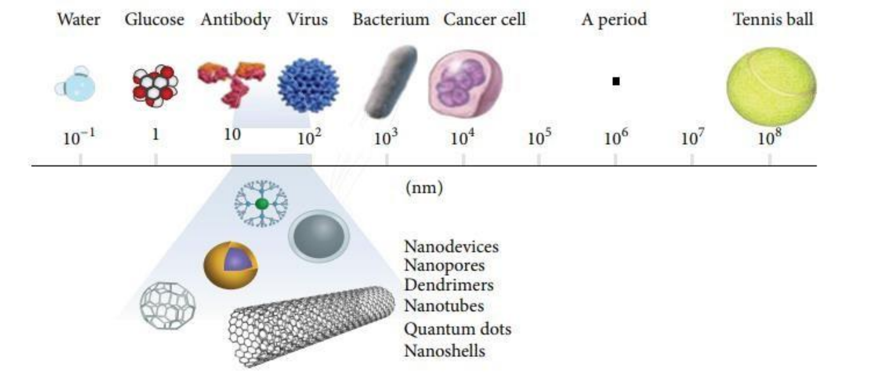
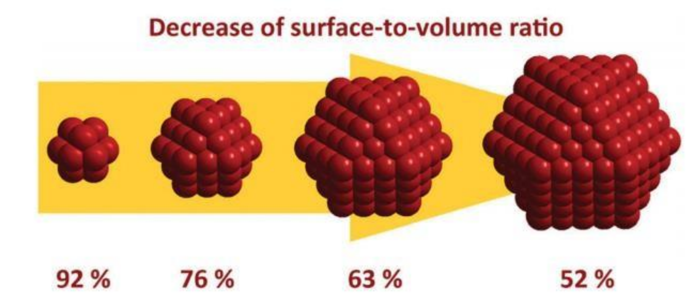
Sous la direction de Simon Tricard (LPCNO)
et Thomas Fernique (LIPN)

Introduction

<u>Nano-objects:</u> materials with at least one dimension that is on the nanometer scale (≤ 100 nm) → Physical and chemical properties ≠ bulk material



M. T. Amin, A. A. Alazba, and U. Manzoor, **A Review of Removal of Pollutants from Water/Wastewater Using Different Types of Nanomaterials**, *Hindawi* **2014**, *24*



P. Sonstrom and M. Baumer, **Supported colloidal nanoparticles in heterogeneous gas phase catalysis: on the way to tailored catalysts**, *Chem. Phys.* **2011**, *13*, 19270–19284

Many applications

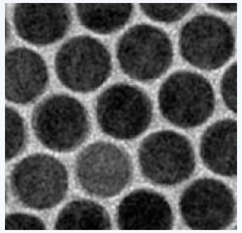
optoelectronics, photovoltaics, photocatalysis, microelectronics, sensors, and detectors

Introduction

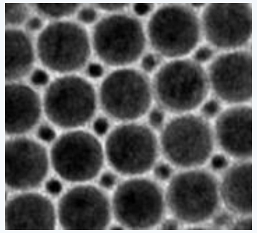
How to arise and control precisely those propoerties ?

Maximization of the interactions between nanoparticles: Assembly in superlattice

Control the organisation: contol the interaction between nanocristals

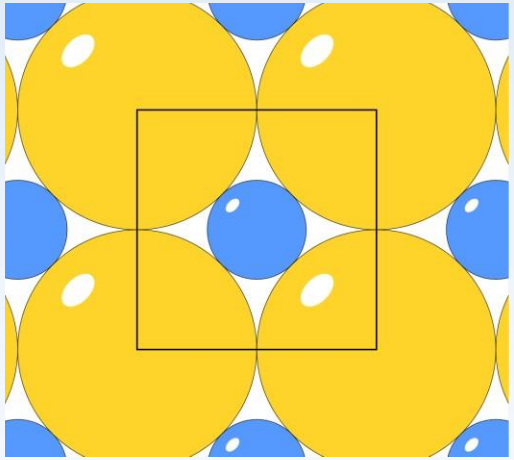


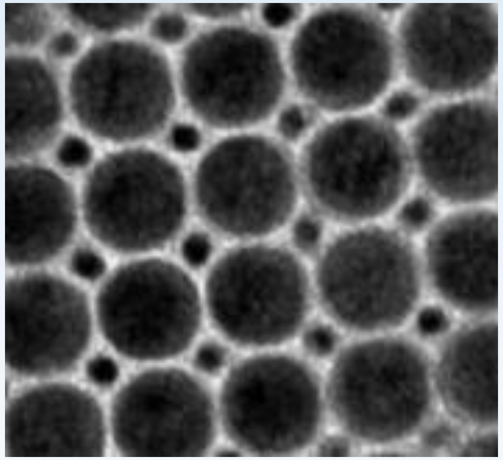
New properties by coupling differents NPs



Purpose of the project

Develop a predictive and rational approach in order to synthesize nanostructured materials, by developing both theoretical and experimental techniques for determining stackings and achieving self-assemblies.





The nine magic ratios and the corresponding compact packings from Kennedy 2004. Figure is adapted from T.Fernique 2019

Taejong Paik, Benjamin T. Diroll, Cherie R. Kagan, and Christopher B. Murray, **Binary and Ternary Superlattices Self-Assembled from Colloidal Nanodisks and Nanorod**, *J. Am. Chem. Soc.* **2015**, *137*, 6662–6669

Self-assembled NPs

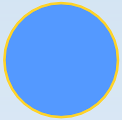
Parameters to control assembly

- Monodispersity !
- Surfactants, ligands
- Assembly method (temperature, pressure, evaporation time, concentration…)
- VdW interactions dicrease with NP's size

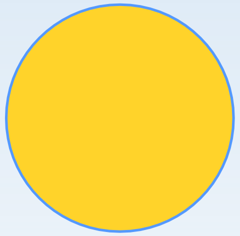
Binary assembly

- $q = \frac{R_S}{R_L}$
- $p = \frac{N_S}{N_S + N_L}$

q | p

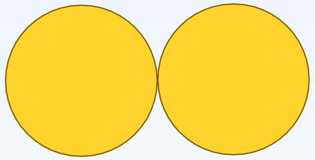


N_S discs of radius R_S

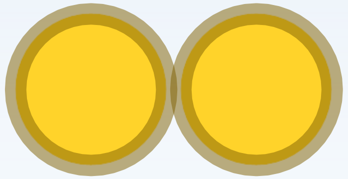


N_L discs of radius R_L

$$q = \frac{R_S}{R_L} \quad \text{and} \quad p = \frac{N_S}{N_S + N_L}$$



Hard-disc model



Nanoparticles with ligand’s shell ?

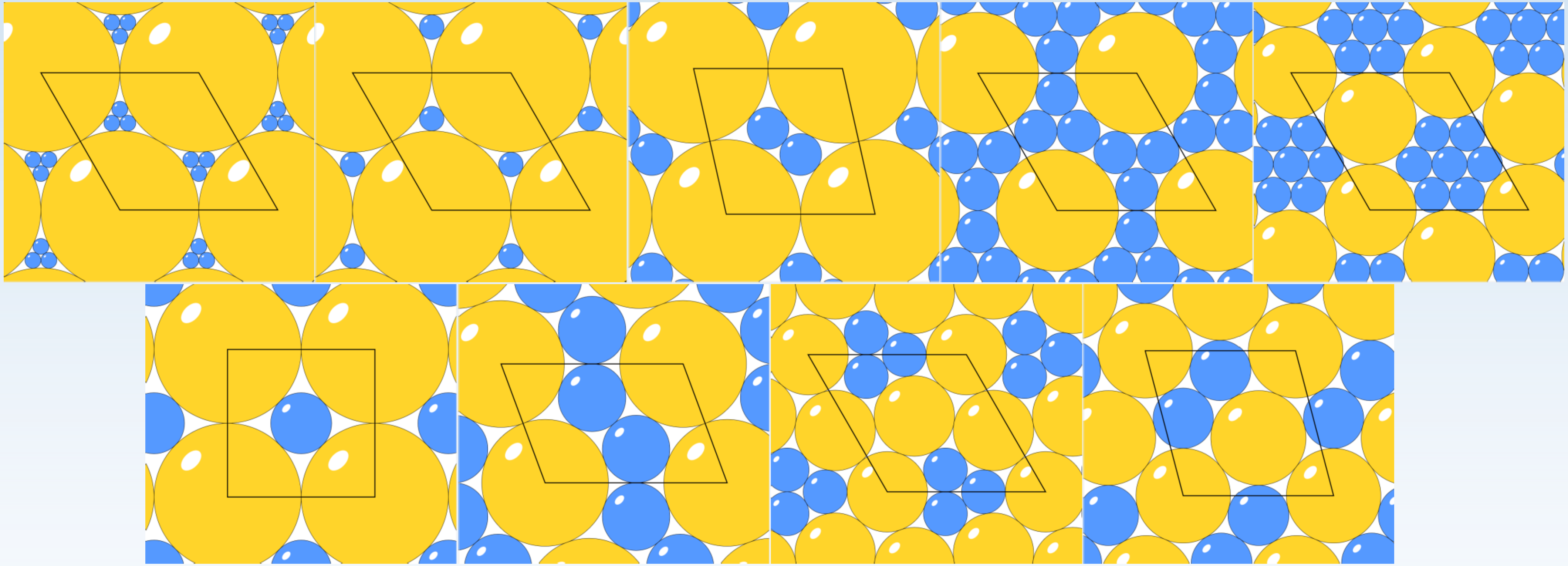
11rr, T2 (AB_6) q_1=0,101…

111, T1 (AB_2) q_2=0,154…

111r, T1 (AB_2) q_3=0,280…

1rr1r, T2 (AB_6) q_4=0,349…

1rrr1, H3 (A_2B_7) q_5=0,386…



q_6=0,414… (AB) 1111, S1

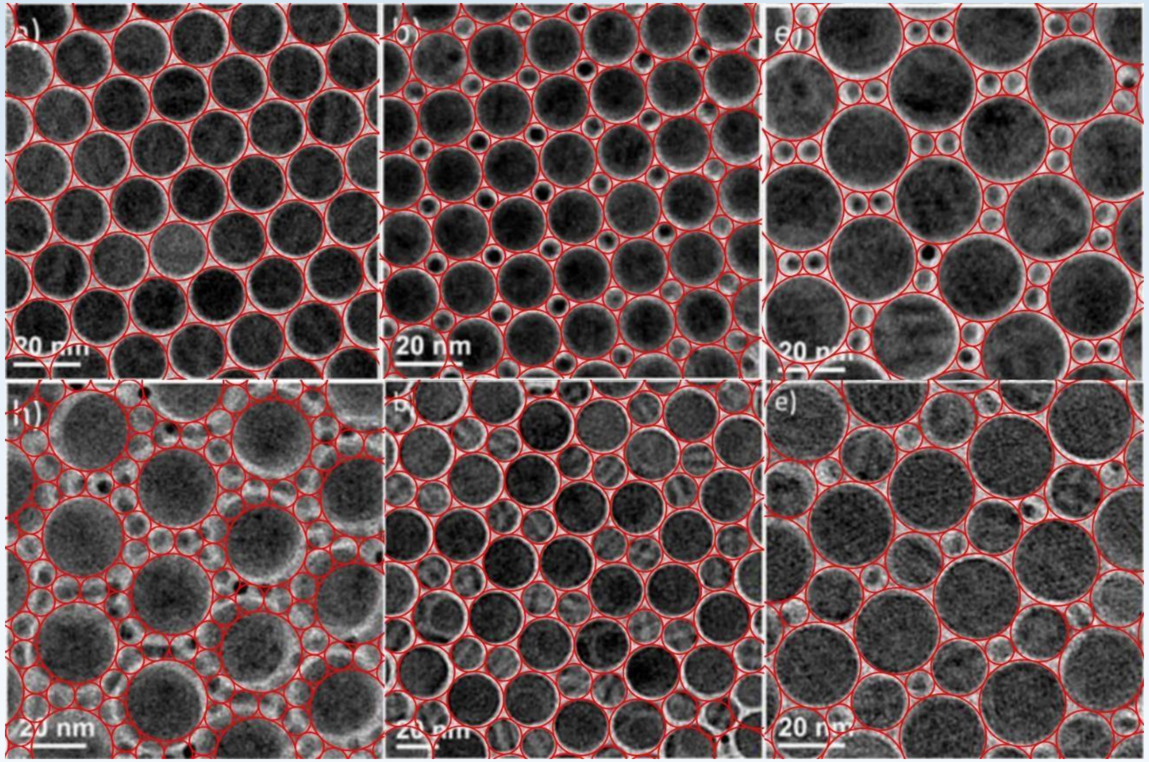
q_7=0,533… (AB_2) 1r1r1, H1

q_8=0,545… (AB) 111rr, H1

q_9=0,637… (AB) 1111r, H2

The nine magic ratios and the corresponding compact packings from Kennedy 2004. Figure is adapted from T.Fernique 2019

Does it work at nanoscale ?



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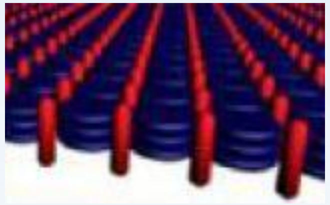
→ Nanodisks and nanorods

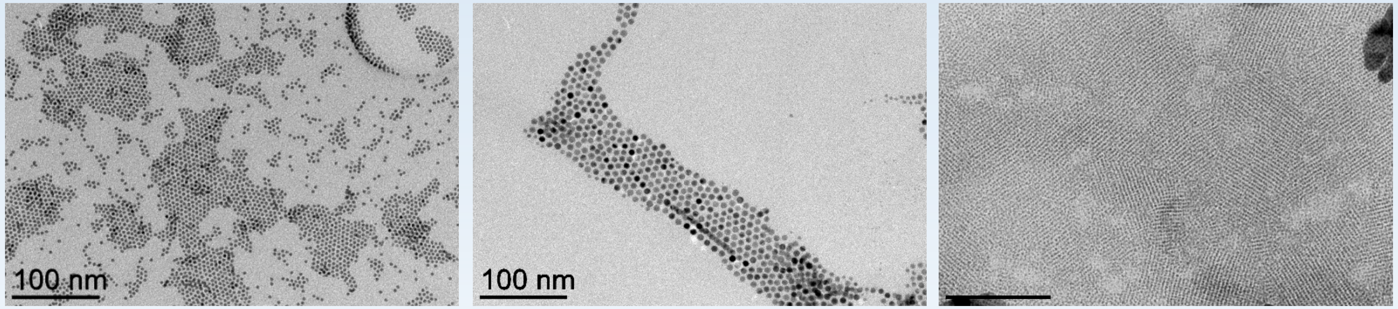


Firsts perspectives

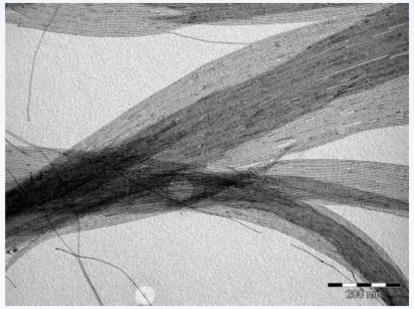
Firsts axis

- Particles with very **small and define sizes**

→ Preliminary results with Ru and Au nanoparticles



- **Nanowires**

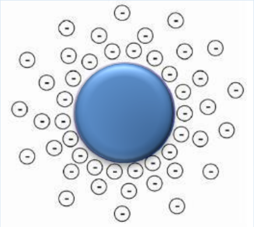


Preliminary results | Ru NPs

Synthesis

$RuCl_3.xH_2O$ + $NaOAc.3H_2O$ → (x °C/min; 150°C; 1,2-propanediol)

Charge stabilisation

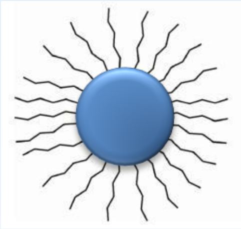


NPs Ru

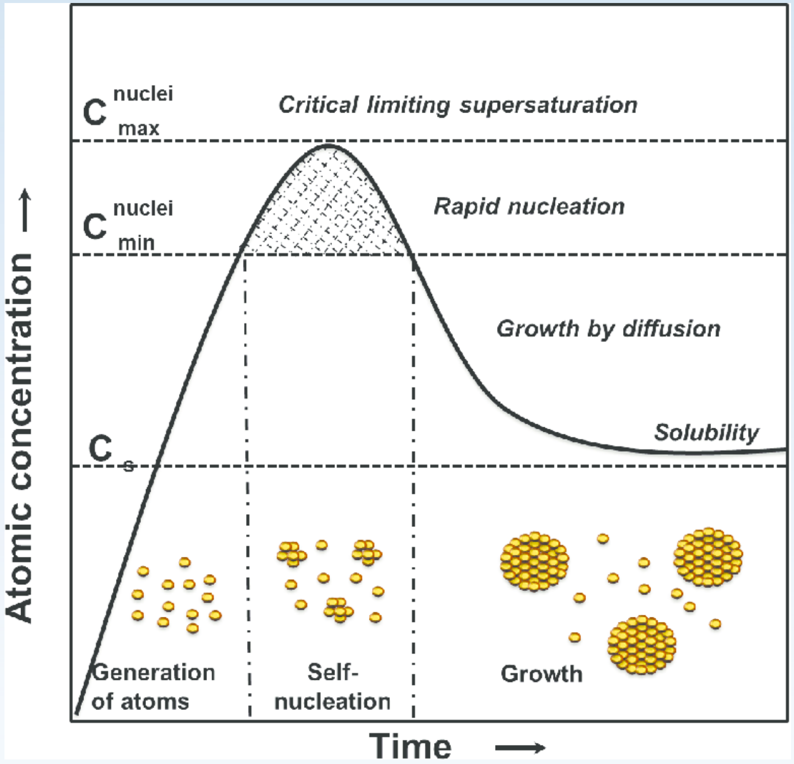
Extraction

NPs Ru (1,2-propanediol) + x HSC_nH_{2n+1} (toluene) →

Steric stabilisation



NPs Ru

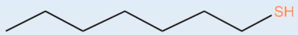


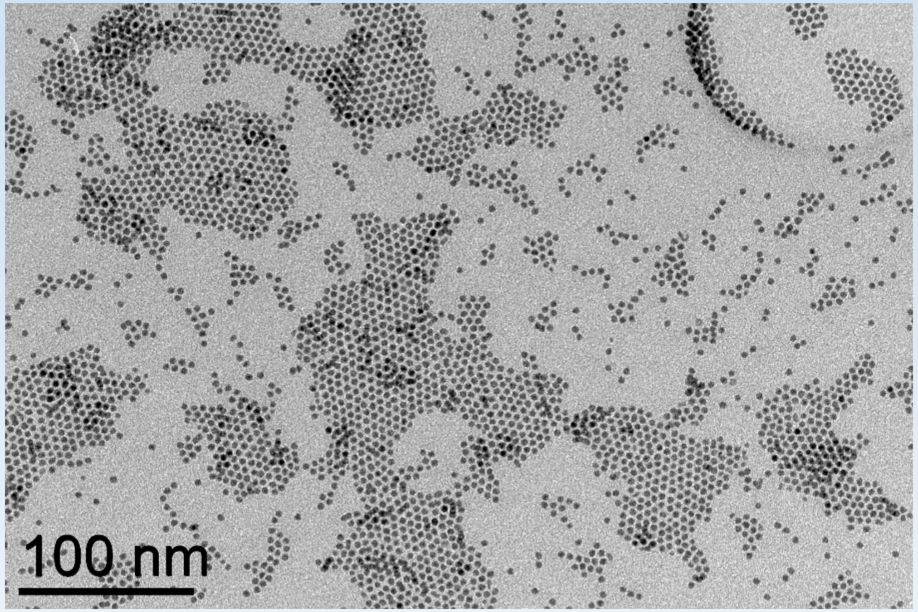
Size control :

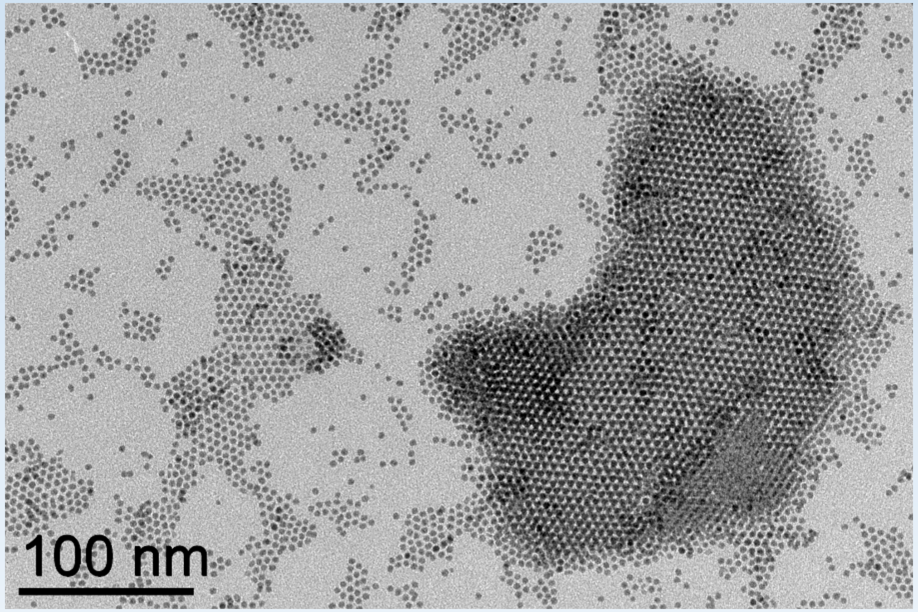
- Temperature and heating velocity
- Precuseur concentration
- $NaOAc.3H_2O$ concentration

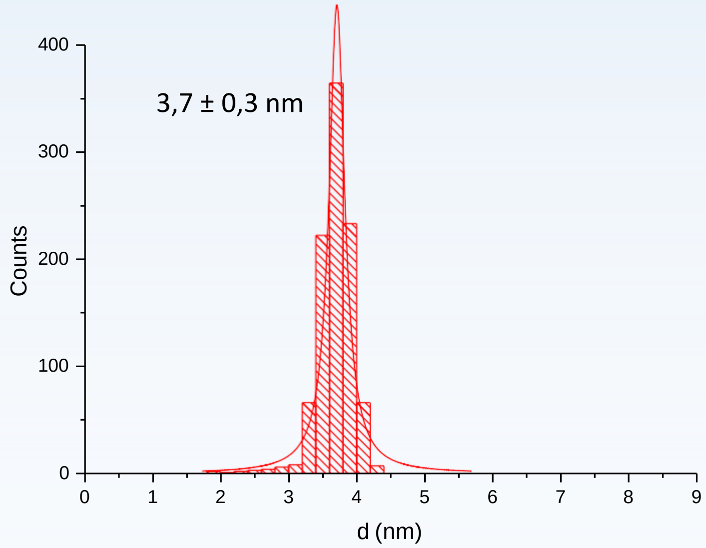
Preliminary results | Ru NPs

Surfactant: heptanethiol





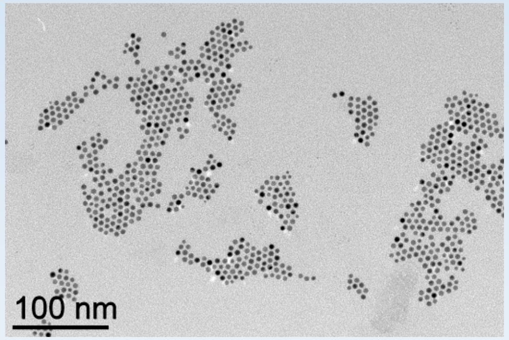
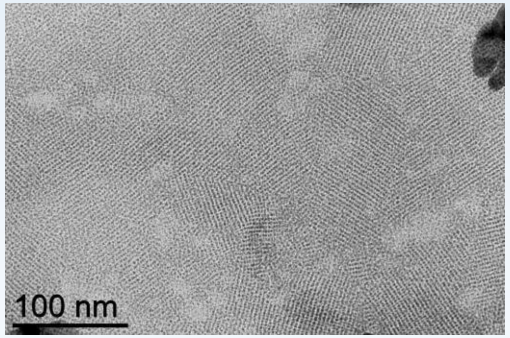




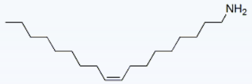
R_b	2,7 ± 0,2 nm
R_c	2,8 ± 0,3 nm
R_d	3,2 ± 0,3 nm
R_e	3,7 ± 0,3 nm

Preliminary results | Au NPs

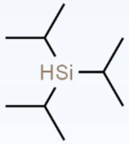
Precurseur + OY + TIPS —Hexane→ Nanoscale solution

	Precurseur	OY	TIPS	Hexane	Nanoscale solution
$HAuBr_4.3H_2O$	10 mM	400 mM	1 M	40 °C	
$HAuCl_4.3H_2O$	20 mM	50 mM	0,75 M	RT	

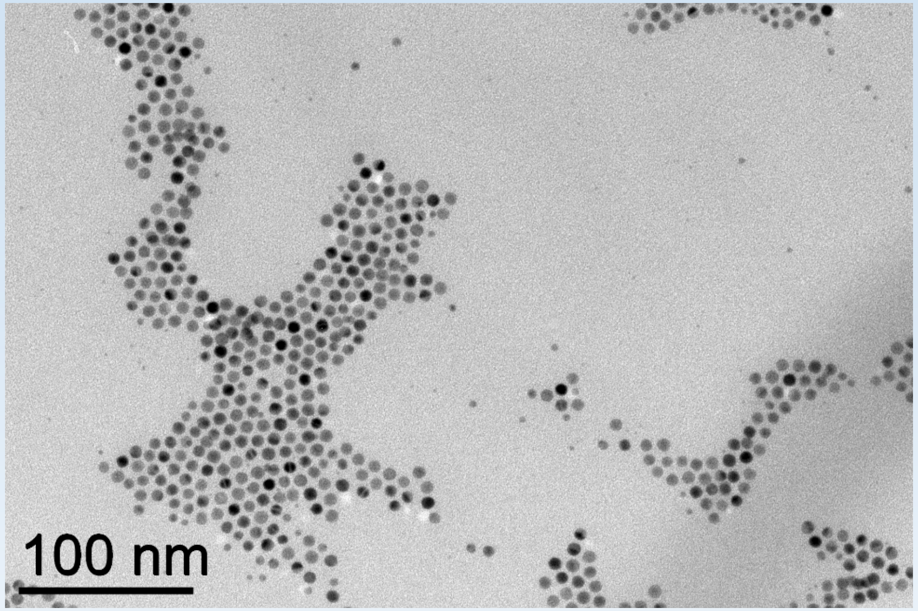
OY: oleylamine

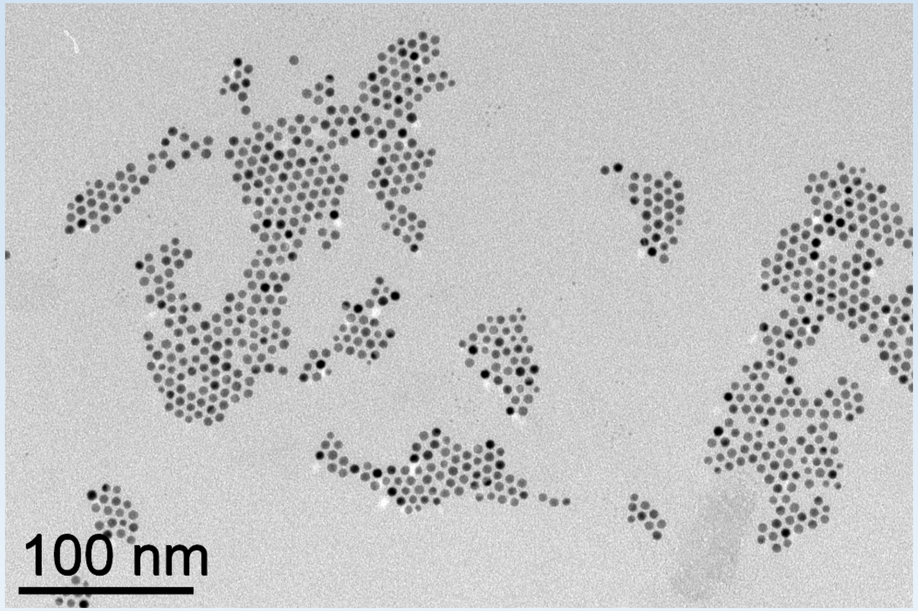


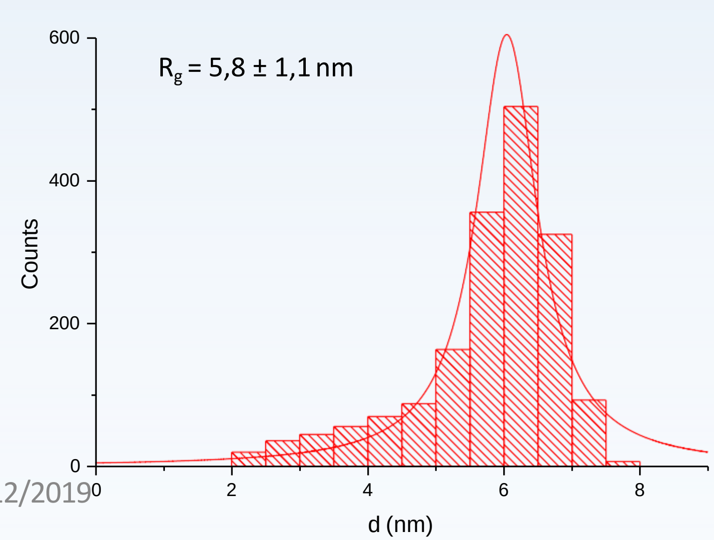
TIPS: triisopropylsilane

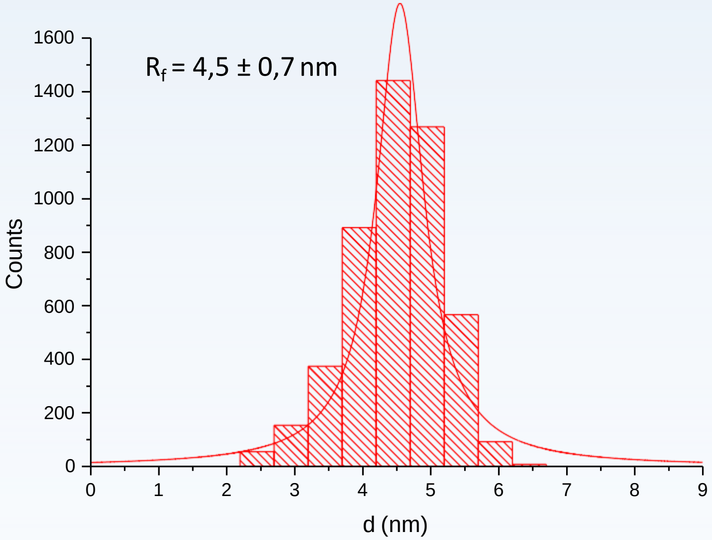


Preliminary results | Au NPs



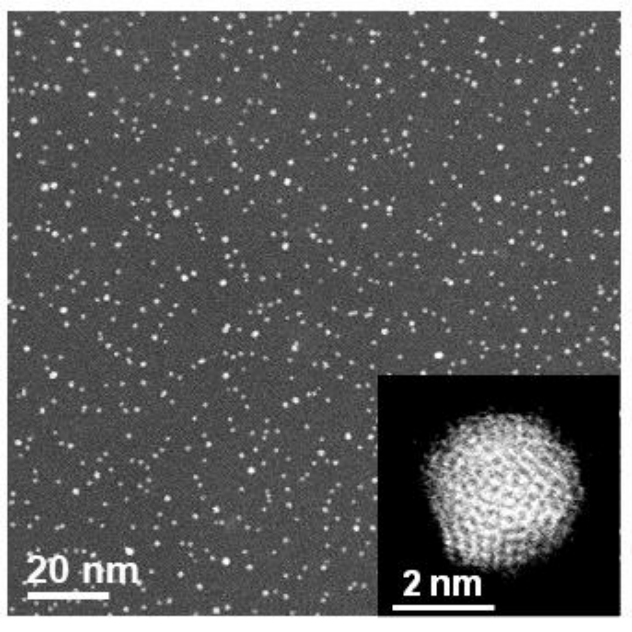


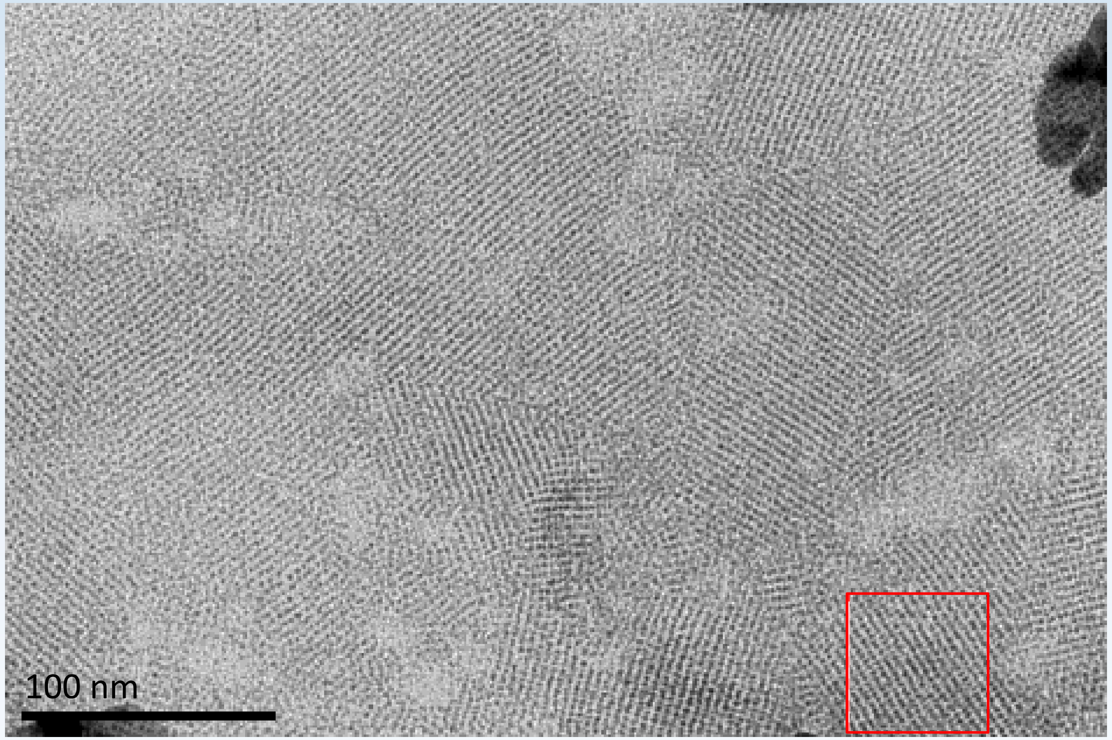




Preliminary results | Au NPs

2 nm gold nanoparticules organised in bcc structure



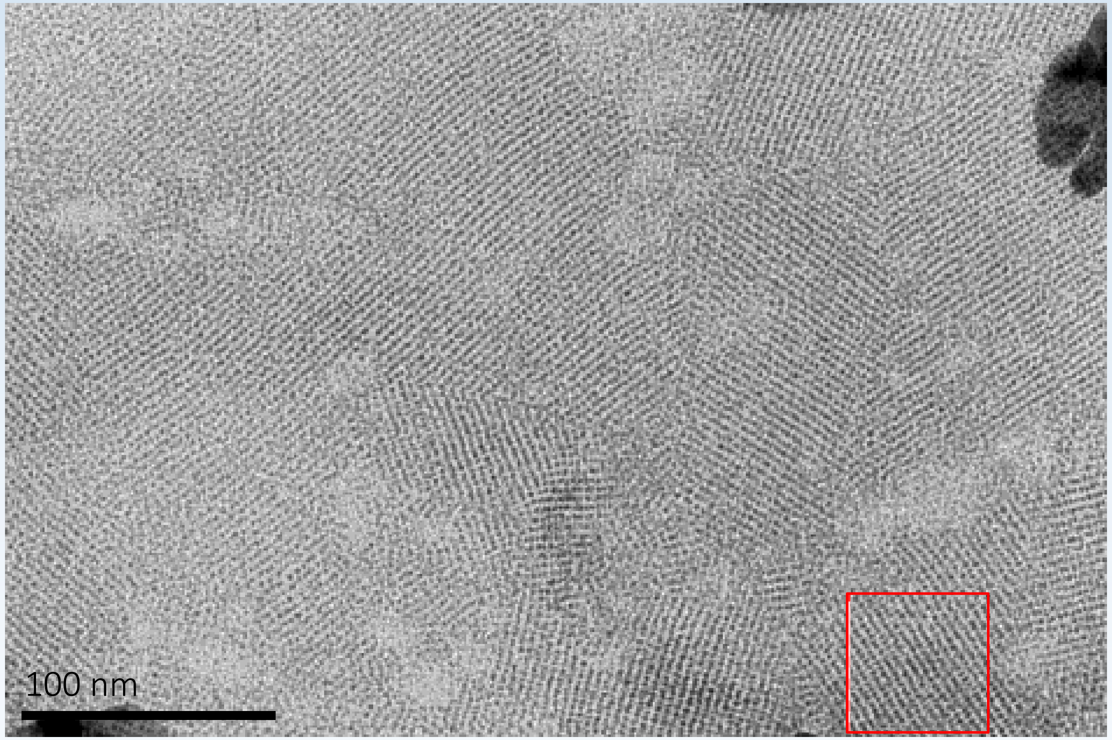


R_g ~ 2 nm

PhD: Ezgi Yldirim

Preliminary results | Au NPs

2 nm gold nanoparticules organised in bcc structure



R_a ~ 2 nm

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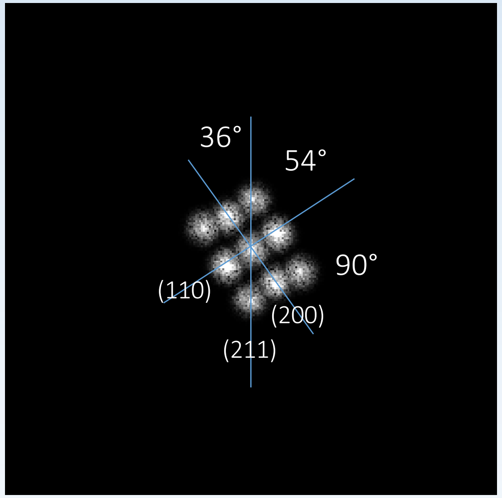
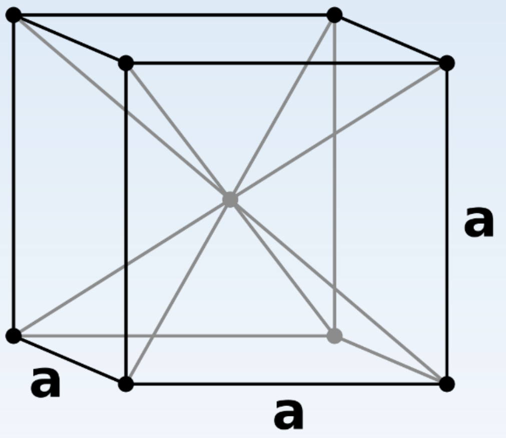


Classical zone axis for bcc structures



To binary systems

$q=\frac{R_S}{R_L}$	numerical	exact	name	stoichiometry
q_1	0.1010205144	$5-2\sqrt{6}$	*11rr, T2*	AB_6
q_2	0.1547005384	$2\sqrt{3}/3-1$	*111, T1*	AB_2
q_3	0.2807764064	$(\sqrt{17}-3)/4$	*111r, T1*	AB_2
q_4	0.3491981862	$\sin\left(\frac{\pi}{12}\right)/\left(1-\sin\left(\frac{\pi}{12}\right)\right)$	*1rr1r, T2*	AB_6
q_5	0.3861061049	$\left(2\sqrt{3}+1-2\sqrt{1+\sqrt{3}}\right)/3$	*1rrr1, H3*	A_2B_7
q_6	0.4142135624	$\sqrt{2}-1$	*1111, S1*	AB
q_7	0.5332964167	$8q^3+3q^2-2q-1=0$	*1r1r1, H1*	AB_2
q_8	0.5451510421	$(7+4\sqrt{3})q^4+(20+12\sqrt{3})q^3+(6+4\sqrt{3})q^2-(20+4\sqrt{3})q+3=0$	*111rr*	AB
q_9	0.6375559772	$q^4-10q^2-8q+9=0$	*1111r, H2*	AB

- size ratio *q* must correspond to one of the 9
- Same surfactant at the surface of the NPs (transfer between oleylamine and heptanethiol)
- Nanoparticles very monodisperse (centrifugation)
- Work on the assembly method

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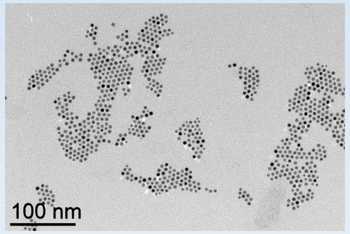
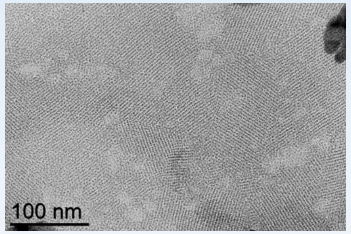
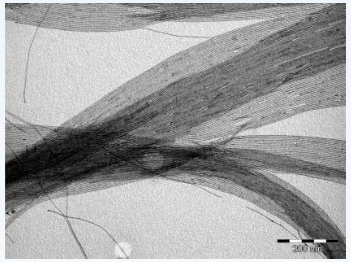
R_S/R_L	R_a	R_b	R_c	R_d	R_e	R_f	R_g
R_a	1	0,741	0,714	**0,625**	**0,541**	**0,444**	**0,345**
R_b	-	1	0,964	0,844	0,730	**0,600**	**0,466**
R_c	-	-	1	0,875	0,757	**0,622**	**0,483**
R_d	-	-	-	1	0,865	0,711	**0,552**
R_e	-	-	-	-	1	0,822	**0,638**
R_f	-	-	-	-	-	1	0,776
R_g	-	-	-	-	-	-	1

$q_4 < R_{min}/R_{max} < q_9$

Binary systems with nanowires

- Gold nanowires:

Precurseur + OY + TIPS —Hexane→ Nanoscale solution

Precurseur		OY	TIPS	Hexane	Nanoscale solution
$HAuBr_4.3H_2O$	10 mM	400 mM	1 M	40 °C	
$HAuCl_4.3H_2O$	20 mM	50 mM	0,75 M	RT	
$HAuCl_4.3H_2O$	10 mM	400 mM	1 M	RT	

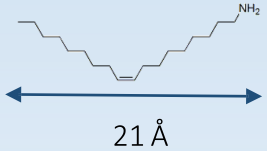
[1] El Said A. Nouh, Edwin A. Baquero, Lise-Marie Lacroix, Fabien Delpech, Romuald Poteau, and Guillaume Viau, **Surface-Engineering of Ultrathin Gold Nanowires: Tailored SelfAssembly and Enhanced Stability**, *Langmuir* **2017**, *33*, 5456–546

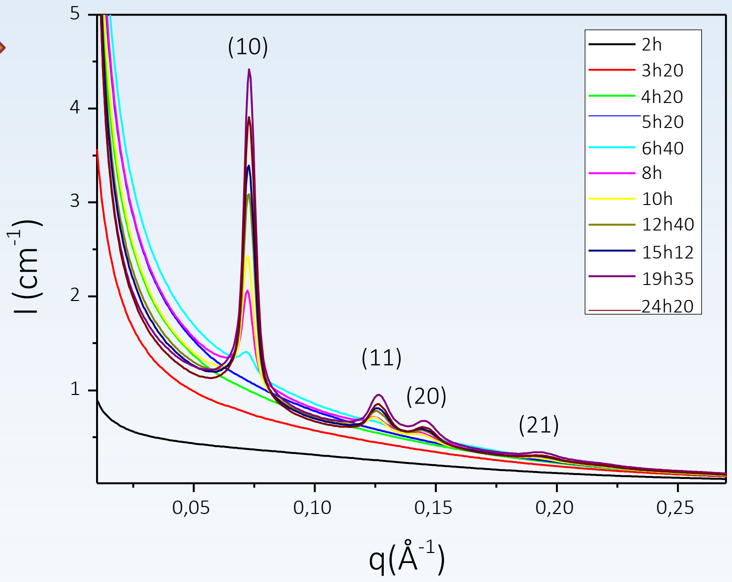
Binary systems with nanowires

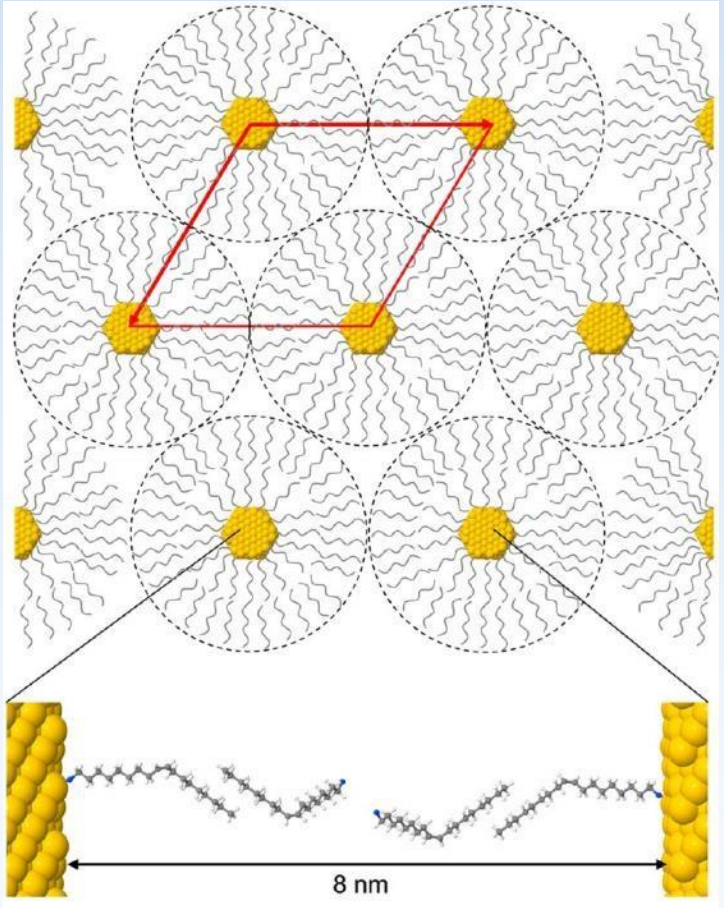
- Gold nanowires:

Diameter ~ 2 nm
Length: few µm[1]

2D hexagonal array:
parameter a = 9.7 nm







2D assembly in one direction: hexagonal compact[2]

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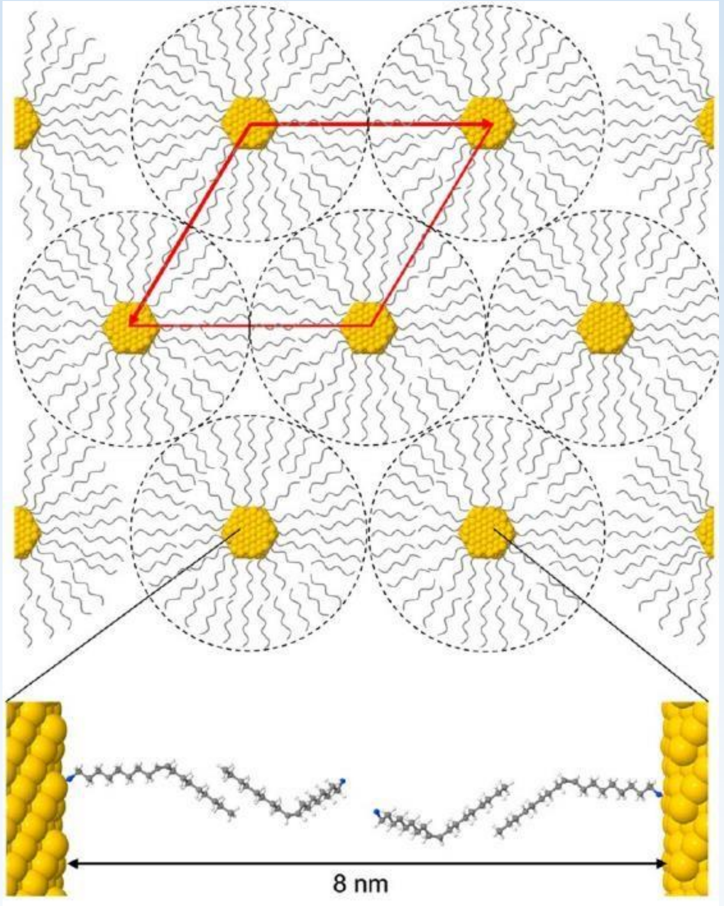
[2] Anaïs Loubat, Marianne Impéror-Clerc, Brigitte Pansu, Florian Meneau, Bertrand Raquet, Guillaume Viau, and Lise-Marie Lacroix, **Growth and Self-Assembly of Ultrathin Au Nanowires into Expanded Hexagonal Superlattice Studied by in Situ SAXS,** *Langmuir* **2014**, *30*, 4005–4012

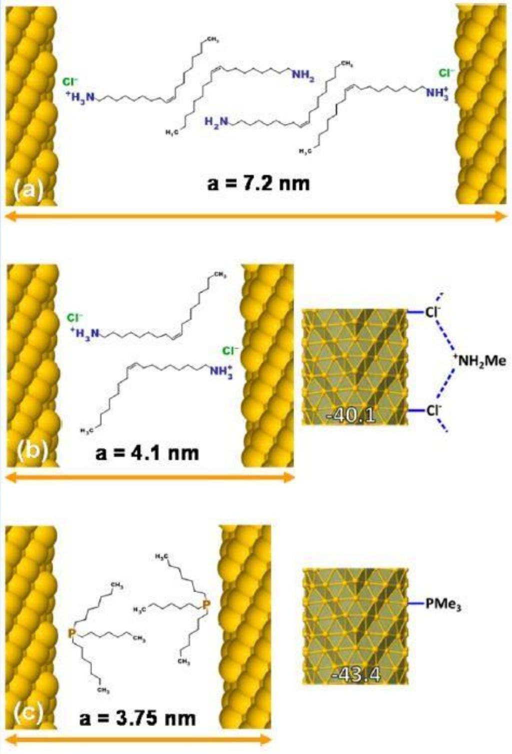
Binary systems with nanowires

- Gold nanowires:

Diameter ~ 2 nm
Length: few µm[1]



2D assembly in one direction: hexagonal compact[2]



Distance between the wires can be adjust by changing the surfactant and/or its quantity[1]

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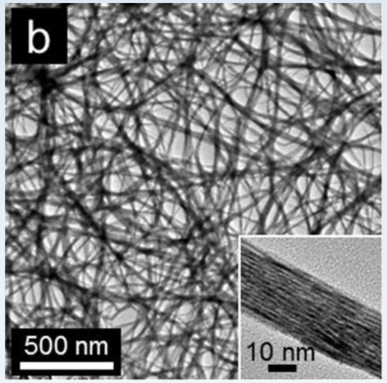
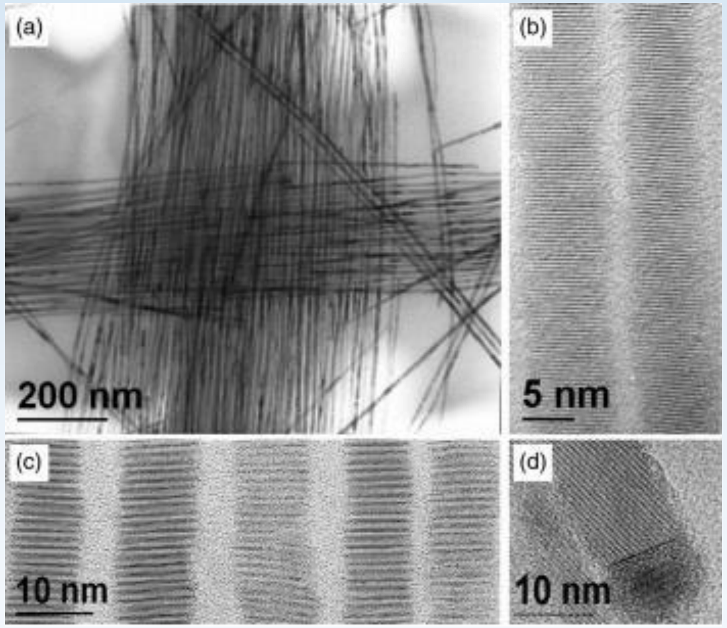
Binary systems with nanowires

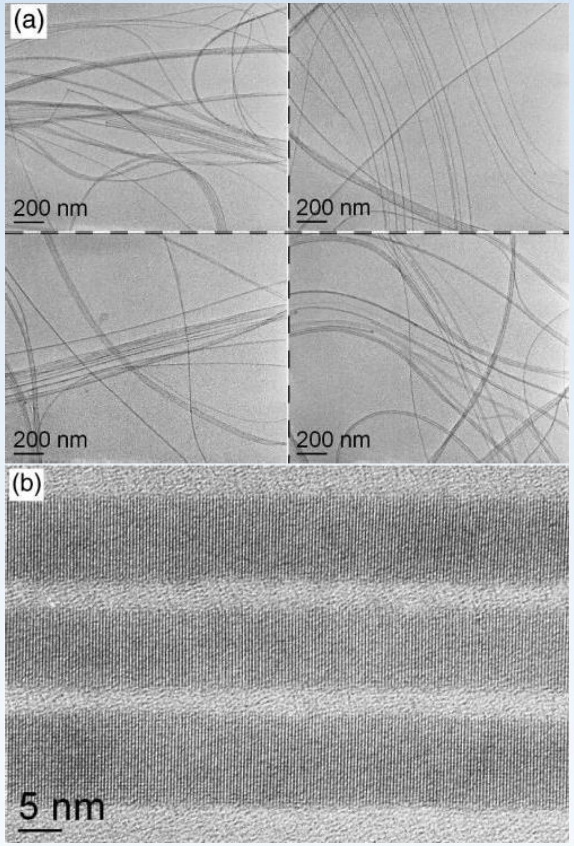
- Other NWs : Pt, CdSe, CdTe



Diameter ~ 3 nm
Length ~ 10 µm
Assembly ~ 30 nm de diamètre[4]



Diameter ~ 7 à 10 nm
Length ~ 1 à 10 µm[5]



Diameter ~ 5 à 10 nm
Length: few µm[6]

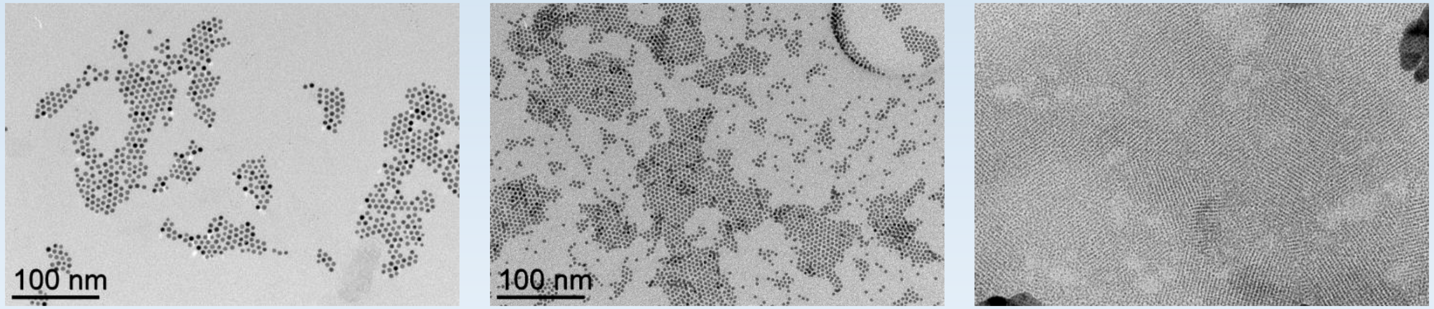
[6] Bao Yu Xia, Hao Bin Wu, Ya Yan, Xiong Wen (David) Lou, and Xin Wang, **Ultrathin and Ultralong Single-crystal Pt Nanowire Assemblies with Highly Stable Electrocatalytic Activit**, *J. Am. Chem. Soc.* **2013**, *25*, 9480-9485
[7] James W. Grebinski, Katherine L. Hull, Jing Zhang, Thomas H. Kosel, and Masaru Kuno, **Solution-Based Straight and Branched CdSe Nanowire,** *Chem. Mater.* **2004**, *16*, 5260-527
[8] Masaru Kuno, Omar Ahmad, Vladimir Protasenko, Daniel Bacinello, and Thomas H. Kosel, **Solution-Based Straight and Branched CdTe Nanowires,** *Chem. Mater.* **2006**, *18*, 5722-5732

Conclusion & perspectives

- Differents NPs with several sizes

Assembly

$q_4 < R_{min}/R_{max} < q_9$



- Work on the way to assemble
- Make binary systems
- Try with nanowires