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Colloidal design of nanoparticles and hierarchical nanostructures

Cyrille Hamon

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Colloidal design of nanoparticles and hierarchical nanostructures

Habilitation à diriger des recherches
de l'Université Paris-Saclay

présentée et soutenue à Orsay, le 7 septembre 2023, par

Cyrille Hamon

Composition du jury

Fabienne Testard DR CEA, IRAMIS, (Gif sur Yvette)	Rapporteuse
Stéphane Parola Professeur, ENS Lyon (Lyon)	Rapporteur
David Portehault DR CNRS, LCMCP (Paris)	Rapporteur
Emmanuelle Lacaze DR CNRS, INSP (Paris)	Examinatrice
Mona Tréguer-Delapierre Professeure, ICMCB (Bordeaux)	Examinatrice
Hynd Remita DR CNRS, ICP (Orsay)	Examinatrice

Titre : Synthèse colloïdale de nanoparticules et de nanostructures

Mots clés : nanoparticules, auto-assemblage, supercristaux, synthèse colloïdale

Résumé : Les développements de demain en nanotechnologie nécessitent des arrangements complexes d'objets de taille nanométrique à un coût raisonnable. Bien que moins établies que d'autres méthodes de fabrication, les approches basées sur les nanoparticules (NPs) colloïdales dépassent les limites intrinsèques des méthodes lithographiques. Les nanoparticules plasmoniques (Au, Ag) sont utilisées ici comme bloc élémentaire car elles présentent des propriétés optiques originales, connues sous le nom de résonance plasmon de surface. La cristallinité de ces NPs peut être bien contrôlée et celles-ci peuvent former des édifices tridimensionnels complexes avec une précision nanométrique sur la distance interparticulaire, appelés supercristaux. En outre, le matériau peut être façonné pour induire de nouvelles propriétés plasmoniques avec un effort de synthèse minimal. Une large gamme de réponse optique peut être obtenue en fonction de l'orientation et de l'arrangement des NPs.

La conception de matériaux plasmoniques colloïdaux est un domaine interdisciplinaire qui doit être envisagé selon une perspective transverse. Outre la physique associée à la réponse optique (génération de chaleur, exaltation de signaux optique...), les nanoparticules sont préparées par des approches chimiques et stabilisées par une couronne de ligands donnant des propriétés comme la solvatation ou bien encore la stabilité colloïdale et dont la chimie de surface régit les interactions. Selon la technique utilisée pour assembler les nanoparticules, d'autres domaines de la physique doivent être pris en compte tels que le mouillage, l'évaporation, etc. Ce manuscrit présente les efforts déployés ces cinq dernières années pour façonner les NPs plasmoniques et pour contrôler leur arrangement à différentes échelles spatiales.

Title : Colloidal design of nanoparticles and hierarchical nanostructures

Keywords : plasmonic nanoparticles, self-assembly, supercrystal, colloidal synthesis

Abstract : Future developments in nanotechnology require the complex arrangements of nano-sized objects at a reasonable cost. Although less established than other manufacturing standards, approaches based on colloidal nanoparticles (NPs) are cost-effective and go beyond intrinsic limitation of lithographic methods. Plasmonic nanoparticles (Au, Ag) are used here as building blocks because they can support light-driven collective electron oscillations, known as localized surface plasmon resonance. Interestingly, the crystallinity of such NPs can be well controlled and can often form complex three-dimensional structure with nanometric precision on the interparticle distance, so called supercrystals. Moreover, various self-assembly approaches can produce a large variety of new plasmonic nanostructures with a minimal synthetic effort. A large range of plasmonic response can be obtained depending on the orientation and nanostructuring of the NPs.

For instance, plasmon coupling can take place when AuNPs enter into proximity, resulting in amplified electromagnetic fields at the junction between NPs, the enhancement being more intense as the distance decreases. Devising colloidal plasmonic materials is a highly transverse field that should be seen from an interdisciplinary perspective. Besides the rich physics associated with the optical response (e.g. heat generation, carrier recombination), the nanoparticles are prepared by wet chemical approaches and stabilized by a soft corona of ligands giving properties like solvation, colloidal stability, surface chemistry and often tunable interaction. Depending on the technique used to assemble the nanoparticles, other field of physics should be taken into account such as wetting, capillary flows and so forth. This manuscript presents efforts towards shaping plasmonic NPs as well as controlling their arrangement at different length scale.

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CURRICULUM VITAE

Cyrille Hamon

CNRS researcher (section 15)

Age 35. 2 children.

CNRS junior research scientist – *Laboratoire de Physique des Solides (LPS), UMR 8502, Université Paris-Sud.*

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Research activities

- Since 10.2017** **CNRS junior research scientist** (Chargé de recherche classe normale) – *Laboratoire de Physique des Solides – Université Paris-Sud –MATRIX* group [group website](#)
Topics: Synthesis and self-assembly of nanoparticles. Confinement related effects
Techniques: colloidal chemistry, small angle X-Ray scattering, Raman spectroscopy.
- 02.2016 - 04.2017** **Post-doctoral researcher** – Matière et systèmes complexes, *Université Paris Diderot* [group website](#)
Title: Detection of zinc in the Seine river
Techniques: colloidal chemistry, microfluidics, Raman spectroscopy.
- 01.2014 - 01-2016** **Post-doctoral researcher** – *CIC Biomagune, San Sebastian, Spain* [group website](#)
Title: Self-assembly of plasmonic nanoparticles for biosensing
Techniques: colloidal chemistry, Raman spectroscopy.
- 10.2010 - 10.2013** **PhD (Chemistry)** – Institut de Chimie de Rennes, *Université de Rennes 1*
Defense the 11st of october 2013. [Link toward manuscript](#)
Presented in front of the jury composed of :
Peter Reiss (Directeur de recherche CEA, rapporteur)
Serge Ravaine (Professeur au CRPP, rapporteur)
Eric Lafontaine (Représentant DGA, examinateur)
Serge Palacin (Directeur de recherche CEA, examinateur)
Oleg Gang (Chercheur, Brookhaven national laboratory, examinateur)
Philippe Hapiot (Directeur de recherche CNRS, examinateur)
Pascale Even-Hernandez (Maîtresse de conférence, co-directrice de thèse)
Valérie Marchi (Directrice de recherche CNRS, directrice de thèse)
Title: Préparation et auto-assemblage de nanobâtonnets fonctionnalisés appliqués à la photo-oxydo-réduction catalytique
Techniques: colloidal chemistry, photocatalysis

Fellowship and awards

2020: Junior chair of LABEX Palm on the “Self-Assembly of Nanoparticles in Confinement”

2017: CNRS permanent position

2014-2015: Post-Doc fellowship from DGA

2010-2013: PhD fellowship from CNRS and DGA

RESPONSIBILITY AND SCIENTIFIC ANIMATION

2022-2027: elected member of CNRS section 15 comity (CoNRS, college B1).

2020-now: substitute member of the direction comity of LPS.

2018-now: organizer of the soft matter seminars at LPS (about 20 seminars per years)

<https://www.lps.u-psud.fr/spip.php?rubrique211&lang=fr>

FUNDING >650k€, including >500k€ as main proposer

Year	Source	Type	Amount (k€)
2022	Labex PALM (PI)	Post-doc (24m)	105
2022	ANR (local coordinator)	Post-doc (18m)	130
2022	CNRS IEA	mobility	10
2022	IDA (U. Paris-Saclay)	consumables	7
2021	METSA	experiment	5
2021	ANR (participation)	PhD	110
2021	SOLEIL (Main proposer)	experiment	
2020	METSA	experiment	5
2020	Labex PALM	Junior Chair	106
2019	University P. Sud	equipment	4
2019	University P. Sud	visiting professor (J. Perez-Juste)	3
2018	LPS	equipment	30
2018	Mi-lourd CNRS	equipment	50
2017	Chinese Schorlanship Council	PhD (4 years)	110
2017	LPS	equipment	25
2014	DGA	post-doc (1 year)	60

+ Experiments on synchrotron several times a year

ONGOING COLLABORATION (ONLY WITH PUBLICATION)

Group or name	Nature of the collaboration	Institute/University	Country	Publication (n° refer to the list)
STEM group	STEM-EELS	LPS	France	17, 25, 28, 33
Theory group	Computer simulation	LPS	France	29

Bruno Palpant	Transient Absorption Spectroscopy	CentraleSupélec	France	23, 30
Damien Alloyeau	Environmental TEM	University of Paris	France	17, 20, 22
Pierre-François Brevet	Non-linear optics	Université Claude Bernard Lyon 1	France	32
Thomas Bizien	SAXS	SOLEIL synchrotron	France	18, 29
Andras Deak	Self-assembly	Hungarian Academy of Sciences	Hungary	35
Eric Hill	MD simulation, synthesis	Hamburg University of Technology	Germany	25, 31
Colloid chemistry group	Self-assembly	University of Vigo	Spain	24
Andrey Chuvilin	FIB-SEM	CIC Nanogune	Spain	24, 29

Doctoral supervision skills

Students are essential for the success of research in laboratories. I co-directed the PhD thesis of Jieli Lyu with Doru Constantin and she has defended successfully in 07/2022. Her research works have been already published in seven peer-reviewed journals and one more is in preparation. She is currently looking for a lecturer position in China. Since my recruitment at CNRS, I also co-supervised another PhD student (Karin El-Rifaii), one post doc and four M2 students, which all pursued their studies with a PhD. I am currently co-supervising one PhD student with Marianne Impéror-Clerc (Jules Marcone, the PhD just started) and I will recruit two post-docs in late 2022.

I am actively looking for students to conduct researches. Besides applying regularly for calls for proposals, I coach students every year for the doctoral school competition. Otherwise, I am currently participating or have participated to individual monitoring boards for three PhD students. Moreover, I already participated to the reviewing board for the defense of M2 students and once for a PhD thesis.

As a final point, I would like to spend a few words on what I consider a fundamental ingredient of a “good science”: a friendly lab environment, fertile for the creation of good networking is crucial for the development of research projects. I am trying to drive this at my level by organizing the soft-matter seminars at LPS on a weekly basis as well as “welcome days” for PhD students and post-docs every year, the latter including a buffet to discuss in a friendly atmosphere. Same arguments hold true on a wider scale: a major part of the work was possible thanks to external collaborations with groups in Paris Saclay University and abroad. A part of my work schedule thus consists in maintaining those collaborations active as well as finding new ones.

Details of the supervision

Period	Level	Name	Publication (numbers refers to the publication list)	% of supervision
2023-2024	Post-Doc	Rahul Nag	-	100%
2022-2024	Post-Doc	Claire Hotton	-	50%
2022-2025	PhD	Jules Marcone	37	50%
2018-2022	PhD	Jieli Lyu	17, 18, 21, 22, 29, 32, 36	50%
2018-2021	PhD	Karin El-Rifaii	27	10%
2020-2022	Post-Doc	Wajdi Chabaani	29, 37	80%
2023	M2	Jaime Gabriel Trazo	-	50%
2022	M2	Jianan Qian	-	80%
2021	M2	Samantha Roque	-	100%
2019	M2	Kinanti Aliyah	17	80%
2021	M1	Masa Johar	-	100%

Member of thesis jury

n°	Name of the candidate	Supervisor	Role in the jury	date	location
1	Nouha El Amri	Kevin Roger	examineur	07/02/2022	LGC (Toulouse)

Scientific production**37 articles in international peer-reviewed journals (20 at CNRS)**

- ❖ 38% first author, 18% last author, 47% corresponding author (Web of Science stat)
- ❖ >1000 citations, h index 14 (google scholar)
- ❖ 3 book chapters
- ❖ >50 articles reviewed for the American Chemical Society, Wiley and Elsevier

Communication (since CNRS)

- ❖ Oral presentation in 8 international conferences (2 invited)
- ❖ Oral presentation in 7 national conferences (4 invited)
- ❖ 11 invited seminars

Detailed list of publications

37. Jules Marcone, Claire Goldmann, Wajdi Chaâbani, Marianne Impéror-Clerc, Doru Constantin,* and Cyrille Hamon*, Polymorphous packing of pentagonal nanoprisms. *Nano Lett.* **2023** in press

36. Jieli Lyu, Claire Goldmann, Cyrille Hamon* and Doru Constantin*, Extracting the morphology of gold bipyramids from small-angle X-ray scattering experiments via form factor modelling. *J. Appl. Crystallogr.* **2023** in press
35. D. P. Szekrényes, C. Hamon, D. Constantin and A. Deák. Formation of kinetically trapped small clusters of PEGylated gold nanoparticles revealed by the combination of small-angle X-ray scattering and visible light spectroscopy *Soft Matter* **2022** Vol. 18 Issue 43 Pages 8295-8301
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33. Goldmann, C.; Li, X.; Kociak, M.; Constantin, D.*; Hamon, C.*, Longitudinal and Transversal Directed Overgrowth of Pentatwinned Silver Nanorods with Tunable Optical Properties. *J. Phys. Chem. C* **2022**. DOI: 10.1021/acs.jpcc.2c02846
32. Lyu, J.; Rondepierre, F.; Jonin, C.; Brevet, P.-F.*; Hamon, C.*; Constantin, D.*, Shape-Controlled Second-Harmonic Scattering from Gold Nanotetrapods. *J. Phys. Chem. C* **2022**, 126 (23), 9831-9835.
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29. Lyu, J.; Chaabani, W.; Modin, E.; Chuvilin, A.; Bizien, T.; Smallenburg, F.*; Imperor-Clerc, M.*; Constantin, D.*; Hamon, C.*, Double-Lattice Packing of Pentagonal Gold Bipyramids in Supercrystals with Triclinic Symmetry. *Adv. Mater.* **2022**, 34 (21), e2200883.
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SOLEIL: <https://www.synchrotron-soleil.fr/fr/actualites/jeu-de-rtetris-avec-des-bipyramides-pentagonales-allongees-quand-la-nanochimie-rencontre>
28. Y. Auad,* C. Hamon, M. Tencé, H. Lourenço-Martins, V. Mkhitarian, O. Stéphan, García de Abajo, F. J., Tizei, Luiz H. G., Kociak, M.* Unveiling the Coupling of Single Metallic Nanoparticles to Whispering-Gallery Microcavities *Nano Lett.* **2022**, 22 (1), 319-327.
27. K. El Rifaii,* P. Davidson, L. Michot and C. Hamon,* Gold-clay nanocomposite colloids with liquid-crystalline and plasmonic properties, *Chem. Commun.* **2021**, 57 (80), 10359-10362.
26. Hamon, C.*; Beaudoin, E.; Launois, P.; Paineau, E.*, Doping Liquid Crystals of Colloidal Inorganic Nanotubes by Additive-Free Metal Nanoparticles. *J. Phys. Chem. Lett.* **2021**, 12 (21), 5052-5058.
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Before recruitment at CNRS

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12. G. Bodelón, V. Montes-García, V. López-Puente, E. Hill, C. Hamon, et al. Detection and imaging of quorum sensing in *Pseudomonas aeruginosa* biofilm communities by surface-enhanced resonance Raman scattering. *Nat. Mater.* **2016**, 15, 1203–1211.
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6. C. Hamon, S. Novikov, L. Scarabelli,† L. Basabe-Desmonts,‡,§ and L. M. Liz-Marzán* Hierarchical Self-Assembly of Gold Nanoparticles into Patterned Plasmonic Nanostructures. *ACS Nano*. **2014** 8(10):10694-10703.
5. T. Bizien, P. Even-Hernandez, M. Postic, E. Mazari, S. Chevance, A. Bondon, C. Hamon, D. Troadec, L. Largeau, C. Dupuis, C. Gosse, F. Artzner, and V. Marchi* Peptidic Ligands to Control the Three-Dimensional Self-Assembly of Quantum Rods in Aqueous Media. *Small*. **2014** 10(18):3707-3716.
4. Hamon, C ; Bizien, T ; Even-Hernandez P ; Artzner, F ; Marchi-Artzner, V.* Replacement of CTAB with peptidic ligands at the surface of gold nanorods and their self-assembling properties. *J. Coll. Inter. Sci.*, **2014** 424(0): 90-97
3. C. Hamon, A. Ciaccafava, P. Infossi, P. Even-Hernandez, E. Lojou, V. Marchi.* Synthesis and Enzymatic photo-activity of O₂ tolerant hydrogenase/CdSe@CdS quantum rod bioconjugate, *Chem. Commun.* 2014 50(39):4989-4992. **Journal cover**
2. Ciaccafava, A., Hamon, C., Infossi, P., Marchi, V., Giudici-Ortoni, M.T., Lojou, E.* Light-induced reactivation of O₂-tolerant membrane-bound [Ni-Fe] hydrogenase from the hyperthermophilic bacterium *Aquifex aeolicus* under turnover conditions. *Phys. Chem. Chem. Phys.*, **2013**, 6(5) : 4137-4146.

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BOOK CHAPTERS

3. Eric H. Hill, Christoph Hanske, Cyrille Hamon, Yuebing Zheng Assembly of Plasmonic Nanoparticles 21st Century Nanoscience – A Handbook: Nanophotonics, Nanoelectronics, and Nanoplasmonics (1st ed.). CRC Press. <https://doi.org/10.1201/9780429351617>
2. Liz-Marzán, L. (Ed.). (2020). Colloidal Synthesis of Plasmonic Nanometals (1st ed.). Jenny Stanford Publishing. <https://doi.org/10.1201/9780429295188>
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CONTEXT AND PRESENTATION OF MY RESEARCH ACTIVITY

General introduction to the field

Nanotechnology is a vast field of research that can be seen through the “elephant’s tale”, a child tale, in which several blind men have to guess the elephant’s shape by feeling different parts of the body. For instance, one blind man feeling a leg and another one feeling the belly would either claim that it is a tree or a wall respectively. Likewise, a single person could not describe precisely research in nanotechnology. For instance, a physicist in optics would recognize a gold nanorod as a nano-antenna, a physicist in soft matter would see it more likely as a building block and a chemist would consider it from a synthetic point of view. The “nanotechnology jar” is filled every year by thousands of peer reviewed papers, testifying for the contribution of thousands of (blind) researchers. The works presented in this manuscript focuses on the colloidal design of nanostructures but attempt to connect the parts between nanoparticles design, self-assembly into hierarchical structures though interdisciplinary research.

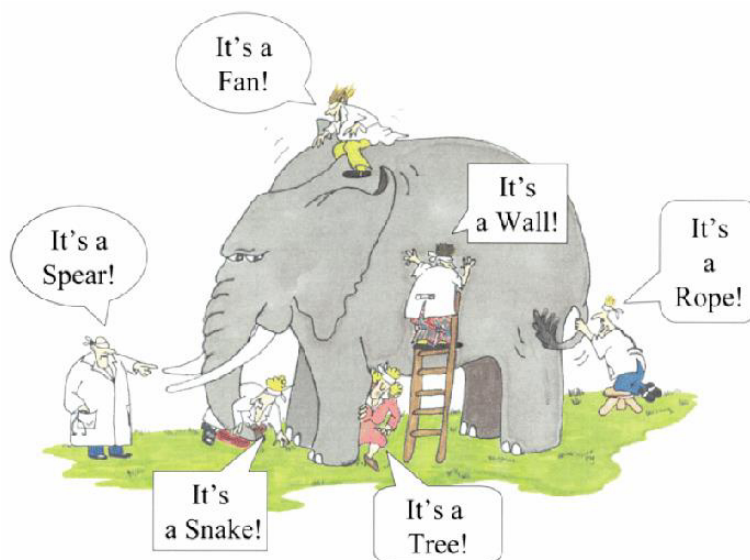


Figure 2-1: The tale of the six blind researchers and the elephant. Image taken from ref¹. This tale is also introduced for nanotechnology there: <https://www.nanowerk.com/spotlight/spotid=5608.php>. The idea for the introduction in this manuscript comes from De Soto’s book “The mystery of capital”.

When the dimensions of a material are reduced on the nanoscale, its properties can be modified in relation to those of the bulk material and are then dominated by finite size effects. Gold is a striking example of such nanoscale confinement related effects. Faraday prepared ruby colored dispersion of gold NPs in 1857 and described the optical properties due to the interaction of finely divided metals with light.² The colored suspensions stand the test of time and are still exhibited at the British Museum. Since this pioneer work, many other protocols

have been proposed that largely improved the level of control over the size of nanoparticles. Notably in 1950, Turkevich and coworkers reduced gold salts with citrate anions forming monodisperse colloids in water, in the range of 10-50 nm.³ Frens refined this protocol in 1973 accomplishing a better size tunability of the particles by adjusting the molar ratio of citrate to gold.⁴ Then, the Brust-Shiffrin method was developed in 1994 in which Au NPs are prepared in a two-phase system leading to nanocrystals as small as 1 nm.⁵ The field continued expanding towards improving size control, monodispersity and develop new methods to control the shape of the NPs. An important leap was the development of colloidal growth method by the groups of Murphy⁶ and El-Sayed⁷ to produce monodisperse gold nanorods by the seed mediated approach. Since then, a vast library of shapes is now accessible by this technique.

Noble metal nanoparticles (NPs) can support light-driven collective electron oscillations, known as localized surface plasmon resonance (LSPR). They exhibit scattering and absorption, which can be influenced by the coinage metal material, environment, size and geometry of the NPs. In the case of spherical Au and Ag NPs, the LSPR are displayed in the visible, around 520 nm (Au) and 400 nm (Ag) but the plasmonic properties can be controlled by varying their shape and size which can be dramatically shifted outside this spectral range. For instance, gold nanorods exhibit two plasmon peaks (transverse and longitudinal) where the position of the longitudinal plasmon peak can be adjusted by the aspect ratio (length/width) of the nanoparticle, from 600 nm to the mid-infrared. The oscillation of the free electron cloud also induces a strong exaltation of the electric field at the surface of the nanoparticles. Those regions of intense optical activity are localized at the tip, interparticle gaps or crevice of NPs and are denoted as hot-spots. The local electromagnetic field in the vicinity of an hot-spot can be several orders of magnitude higher than the incident field at the LSPR wavelength and has been utilized for various plasmon-enhanced optical phenomena, such as surface-enhanced Raman scattering (SERS),⁸ metal-enhanced fluorescence,⁹ or plasmonic photocatalysis.¹⁰ Moreover, the absorption and scattering coefficients of plasmonic NPs are several orders of magnitude higher than those of conventional organic dyes, and therefore they exhibit strong optical properties in the visible, up to the infrared.¹¹ This last feature is particularly interesting for colorimetric sensing such as plasmonic ELISA.¹² Another motivation towards the shape control of plasmonic NPs is to control catalytic performance depending on the facets of the NP exposed. Many developments have been made in plasmonics from nanoparticles for detection, photocatalysis, for medical applications, metamaterials and light confinement.

There is an increasing need to develop methods for integrating NPs in functional materials. Although less established than other manufacturing standards, approaches based on colloidal NPs are cost-effective and go beyond intrinsic limitation of lithographic methods. One can notice that the crystallinity of NPs can be well controlled and can often form complex three-dimensional structure with nanometric precision on the interparticle distance. Moreover, various self-assembly approaches can produce a large variety of new plasmonic nanostructures with a minimal synthetic effort. A large range of plasmonic response can be

obtained depending on the orientation and nanostructuring of the NPs. For instance, plasmon coupling can take place when AuNPs enter into proximity, resulting in amplified electromagnetic fields at the junction between NPs, the enhancement being more intense as the distance decreases.^{13, 14} Devising colloidal plasmonic materials is a highly transverse field that should be seen from an interdisciplinary perspective. Besides the rich physics associated with the optical response (e.g. heat generation, carrier recombination), the nanoparticles are prepared by wet chemical approaches and stabilized by a soft corona of ligands giving properties like solvation, colloidal stability, surface chemistry and often tunable interaction. Depending on the technique used to assemble the nanoparticles, other field of physics should be taken into account such as wetting, capillary flows and so forth. This manuscript presents efforts towards shaping plasmonic NPs as well as controlling their arrangement at different length scale.

Overview of my research activity

In light of these developments, my research in the field revolve around four important aspect that can be represented in **Figure 2-2**. Each stage is a “blind spot” as in the elephant’s tale, wherein interconnection is crucial for the correct interpretation of the results and the best possible input for the identification of directions for improvement.

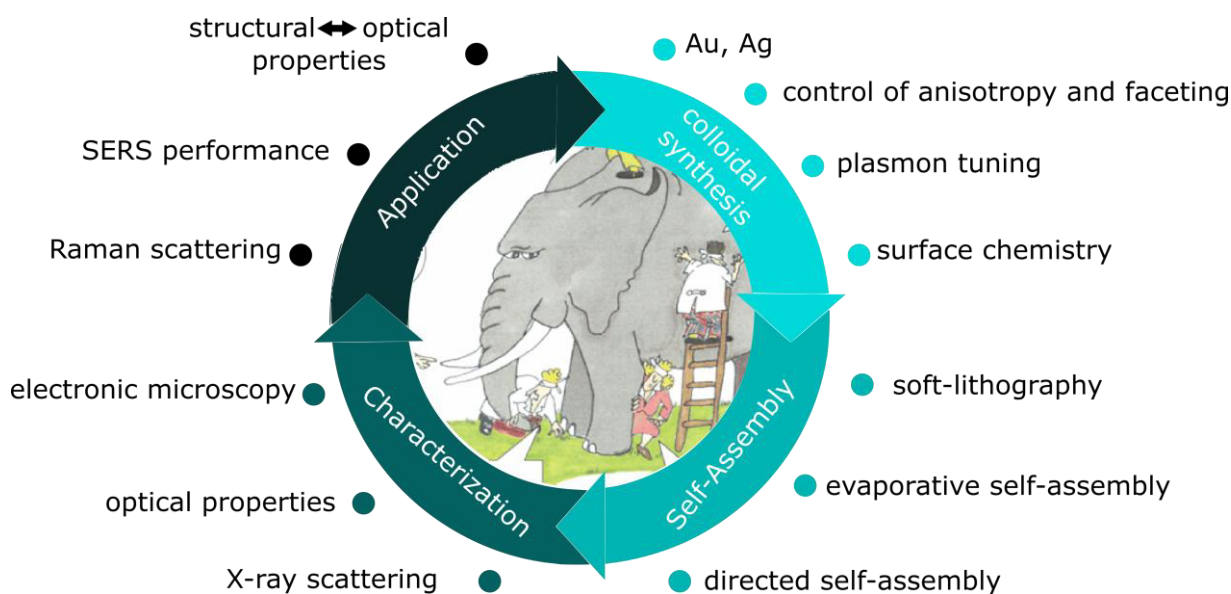


Figure 2-2 : Schematic representation of my research objectives and methods in a loop. Image from ref¹ have been reused.

- 1. Blind spot 1, colloidal synthesis: Achieve high yield synthesis of monodisperse particles with controllable shape and size.** Colloidal plasmonics may be seen as a colossus with promising application in place of the head but that would be sustained by feet of clay. In order to develop technologically efficient nanomaterials, research in colloidal synthesis needs to be consolidated. Although a vast library of particles can be prepared, the underlying growth processes are not fully understood. This is probably

due to the fact that reactants can play different role. For instance, cationic surfactants with halide counterions (e.g. CTAB) are known as particle stabilizers and shape-directing agents, while the halides are known to form complexes with the silver ions,¹⁵ influencing the growth rate. Distinguishing these various functions and studying them properly requires very fine control over the process and the use of advanced techniques (see point n°3) in order to characterize the reaction in detail. Research in this direction may be a leap forward the predictive synthesis of plasmonic nanoparticles and be used as an input for the next stages (**Figure 2-2**).

2. **Blind spot 2, self-assembly: Control the arrangement and long-range organization of NPs.** There are many ways to assemble NPs into higher order structure with different dimensionality, crystallinity and functionality. There is no restriction on the type of NPs (morphology, polydispersity) that can be self-assembled. The corresponding strong optical evolution of the system can lead to application or can be used to probe self-assembly process. Finding simple and efficient ways to arrange, control interdistance and orientation of the NPs still a challenge in the field. Moreover, integration in devices may need precise manipulation of the assembly or propagate the local organization on a larger scale. In this context, developing methods to achieve the hierarchical organization of NPs is also important.
3. **Blind spot 3, characterization: nanoparticles have to be measured precisely in space and time by advanced characterization tools.** Diffraction and spectroscopy techniques can be used to follow NP formation in the growth medium, with high temporal resolution.¹⁶⁻¹⁸ For instance, following NPs synthesis with a millisecond time resolution is feasible by SAXS on synchrotron beamlines. Since I have taken up my CNRS position, this technique (on synchrotron and in-house) have been central in my research activity. However, given their limited spatial resolution and the necessity to develop models, these *in situ* approaches provide an indirect and incomplete overview of the processes. To circumvent this issue, close collaboration with specialist in electronic microscopy is needed. Combining techniques with different strength and weakness as well as modelisation is the key to advance our knowledge in the field.
4. **Blind spot 4, application:** Among the different field of application of plasmonic materials, I focused towards sensing applications which use plasmonic nanoparticles assemblies as Raman scattering transducers. Surface Enhanced Raman Scattering (SERS) spectroscopy can be indeed used to probe molecules of interest in the vicinity of plasmonic hotspots down to the single molecule level. Besides application, reference molecules can be used as local probes of the local electromagnetic field which depends on the arrangement of the NPs and the interparticle spacing. This last feature is a convenient way to probe the collective optical properties of plasmonic nano-assemblies. Although promising, these approaches are still characterized by low technology readiness level and far from being commercially available.

Since my PhD (2013), those four aspects have been the core of my research activity. I did my post-doc in the Luis Liz-Marzán group where plasmonic nanoparticles were assembled to

develop sensitive SERS chemical sensors. The particles were assembled with a crystalline arrangement (supercrystals) in order to improve SERS signals reproducibility and performance. Together with my coworkers, we faced challenges of hierarchical organization and molecular diffusion in plasmonic supercrystals that allowed detecting trace level of analyte in biological samples. Ten publications have been published on these topics, in collaboration with many researchers, including PhD students and post-docs.

In 2017, I joined the MATRIX (Matière et Rayonnement X) group at the Laboratoire de Physique des Solides (LPS). In the continuity of the MATRIX group activities, me and my coworkers explored the complementarity of X-ray diffraction techniques with electronic microscopy ones. I am indebted to Doru Constantin and Marianne Imperor-Clerc for their continuous support in that regard. We believe that the combination of time-resolved techniques shall bring new insight in the understanding of plasmonic material (e.g. NPs, supercrystals) formation. I brought my expertise in colloidal chemistry and I successfully funded the installation of a Raman microscope in 2019 at LPS (the instrument is now fully operational). Therein, I am aiming at developing research revolving around SERS at Paris Saclay University. I already co-supervised a PhD student (Jieli Lyu) on these topics. At this moment, I am co-supervising another PhD student (Jules Marcone) on the self-assembly of anisotropic CoNPs thanks to a mold to guide the evaporation process. The latter project belongs to an ANR project (NimRod) led by Guillaume Viau at LPCNO.

Manuscript organization

For each part, the contribution of students and post-docs is highlighted as well as internal collaboration at LPS (outside MATRIX team) and external collaborators. These works were possible because of discussion, experiments and analysis from MATRIX team members. Since their support is continuous, I do not stress their names in the following. I would like here to acknowledge particularly the contributions of Doru Constantin, Marianne Impéror-Clerc, Erwan Paineau and Patrick Davidson. Although not a member of the MATRIX team, Claire Goldmann (IE CNRS) contributed also a lot to all the works presented in the manuscript.

This manuscript presents researches performed at LPS (since 10/2017), which concerns the wealth of researches around the four blind spots and their interconnection. In chapter 2, I will present our advances in the synthesis of anisotropic bimetallic nanoparticles. Chapter 3 is about the colloidal assembly of the NPs into one-dimensional chains. Chapter 4 concerns the organization of NPs into supercrystals induced by slow solvent evaporation. Chapter 5 presents conclusions and some research perspectives for the next five years.

COLLOIDAL DESIGN OF ANISOTROPIC PLASMONIC NANOPARTICLES

Introduction

One may synthesize nanoparticles by chance by mixing a metallic precursor with a reducing agent but it takes more than luck to control its shape, size, composition and monodispersity in a reproducible manner. In the last two decades, research efforts have pushed forward our understanding of the important parameters that leads to precise nanoparticles synthesis. In the following, I am not going to cover all the field but restrict the discussion on some aspect of nanoparticles synthesis by focusing on the ones I am investigating currently (**Figure 3-1**). I redirect interested readers on recent reviews about seed mediated growth,¹⁹ thermodynamics consideration,²⁰ other type of bimetallic NPs,²¹ one showing the wide range of shapes that can be produced²² and ones more focused about the role of some known shape directing agent.^{23, 24}

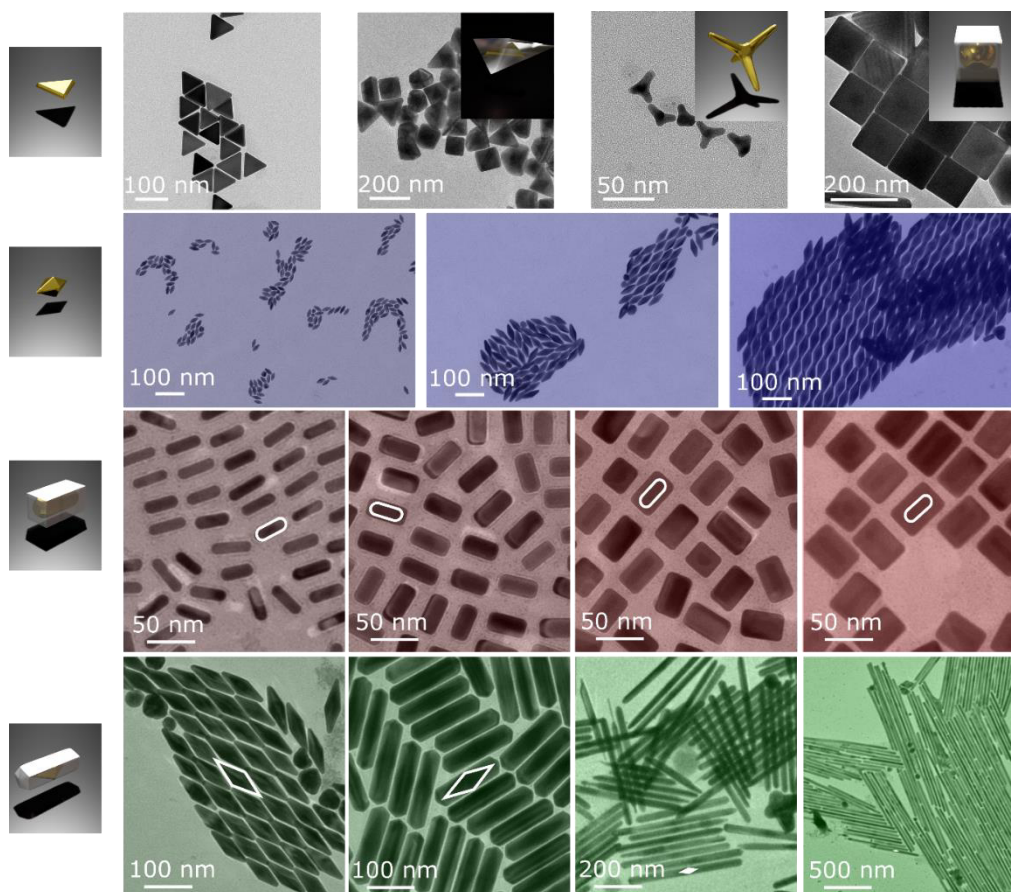


Figure 3-1 : Selection of TEM images of Au or Au@Ag NPs with various morphology that have been synthesized since my arrival at LPS. The colors distinct series of nanocrystal: gold bipyramids of different size (purple), Au@Ag nanorods of varying shell thickness (red), Au@Ag bipyramids of varying shell length (green). Some of the synthesis

have been carried on by myself and mostly by Jieli Lyu (PhD) or Claire Goldmann (IE CNRS).

We are preparing NPs by seed-mediated growth which allow to tune their shape and size with high monodispersity ($\leq 10\%$) and high shape yield (**Figure 3-1**, **Figure 3-2**). This method consists in injecting preformed seeds to a growth solution in order to temporally separate nucleation (formation of the seeds) and growth event. In a typical seed synthesis, a strong reducing agent is used (i.e. NaBH_4) to form the seeds in a few milliseconds. The seeds can be then injected to the growth solution that contains shape directing agents and a “weak” reducing agent (i.e. ascorbic acid (AA)). Indeed, the activation energy for metal reduction onto preformed seeds is significantly lower than that for homogeneous nucleation of seed particles in solution; therefore, it only allows autocatalytic growth of metal atoms on the pre-existing seeds. In a typical synthesis AA reduces Au^{3+} to Au^+ and the addition of seeds finally catalyzes the reduction of Au^+ to Au^0 to generate NPs. Subtle variations of the reaction condition can induce a strong variation of the morphology of AuNPs (**Figure 3-2**). Spheres (quasi spherical) are obtained if no shape-directing agent are introduced. Otherwise, a wide range of polyhedral shapes can be obtained (cubes, octahedra...) as well as smooth isotropic nanoparticles comprising a combination of high index facets. The most common shape directing agent in aqueous seed mediated growth are halides (Cl^- , Br^- , I^-) and silver ions that can preferentially absorb on certain crystal facets. The action of silver ions is known as the silver underpotential deposition in which an Ag^0 adlayer would stabilize high-index facets. This mechanism explains the formation of single crystalline gold nanorods featuring {250} lateral facets or pentagonal gold bipyramids featuring {117} highly stepped facets.²⁵ Other shape directing agent have been described in non-polar solvents such as polyvinylpyrrolidone²⁶ or oleylamine.²⁷ NPs shape control have been described as an interplay between surface diffusion and atom deposition.²⁸ Atoms tends to be deposited at locations that have high surface energies (e.g. vertices, defects, step edges...) and/or on region that are not passivated by capping agent. After deposition, atoms can eventually migrate to other sites or being pinned on its initial deposition by the subsequently deposited atoms defining two growth regimes: site selective growth (i.e. no migration of the atoms after deposition) and conformational growth (migration of the atoms after deposition).¹⁹ Branched particles such as gold tetrapods are an example of NPs obtained within the site selective growth regime whereas gold spheres are obtained within the conformational growth regime (**Figure 3-2**). Experimentally, the rate of atom deposition can be tuned by controlled injection by mean of a syringe pump or manipulating the redox potential of AA with the pH. For instance, increasing the pH increases the redox-potential of AA that allows to speed up the deposition rate of Au in order to obtain gold tetrapods within a few minutes (compared to hours for gold nanorods, **Figure 3-2**). In the case of gold tetrapods, the fast atom deposition is then followed by a slow surface diffusion resulting in a reshaping into sphere within a day. The branches of the tetrapods can be stabilized by post functionalization with thiolated molecule in order to arrest surface diffusion.²⁹ One of our current interest is to stabilize the

tetrapods by other means that would improve surface accessibility compared to functionalization with organic molecules.

Other morphologies can be obtained from seeds comprising stacking fault or twin planes that can be either obtained with iodide (i.e. monotwinned seeds) or citrate followed by a maturation step (i.e. pentatwinned seeds). Those twin planes induce strain in the lattice that increase in the orthogonal direction of the central axis of the seeds. In the case of anisotropic NPs, this strain distribution favor the growth of the NPs in a direction that does minimize the strain.³⁰ The initial symmetry of the seeds is conserved within beveled nanotriangles (from monotwinned seeds) and pentagonal bipyramids (from pentatwinned seeds). Such defect-driven growth mechanisms likely contribute to the formation of the NPs, but chemisorption is also essential to direct the growth of the nanostructure.³¹ For instance, pentatwinned rods instead of pentatwinned bipyramids are obtained without the addition shape directing agent (AgNO_3 in this case).³²

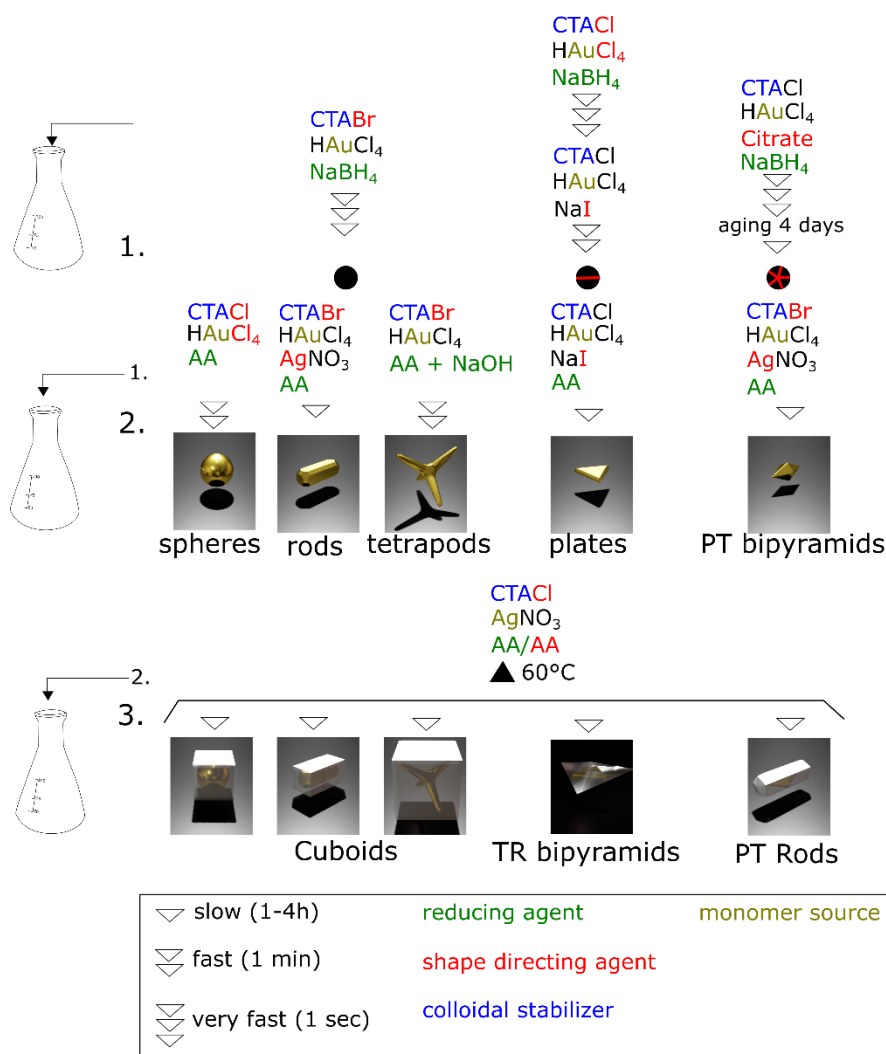


Figure 3-2 : Summary of the experimental conditions used to obtain plasmonic NPs in Figure 3-1.

Depositing silver onto preformed gold NPs have been extensively studied due to the possibility to grow well defined shells (the lattice mismatch between Ag and Au is very small). The reverse procedure (depositing Au on Ag) have been also studied but generally leads to hollow structures through galvanic replacement reaction due to the higher redox potential and the higher degree of oxidation of Au^{3+} compared to Ag^+ . The silver growth onto the gold seeds is directed by two main factors: internal strain in the seeds (twinned defects)³⁰ and preferential chemisorption on certain facets.³¹ For instance, Ag rods have been obtained from gold seeds featuring five twins defects such as decahedra, pentagonal bipyramids and rods. A similar reaction on monocrystalline nanorods or spheres leads to the formation of nanocuboids or nanocubes respectively (**Figure 3-2**). In both cases, Ag {100} facets are stabilized by chlorine ions^{33, 34} and Ag growth is favored in a direction that does not increase the strain distribution in the particles. While chlorine is a known directing agent as other halides, it is also known to form AgCl precipitates that influence growth kinetics due to the relatively slow release of monomers in suspension. Chlorine is introduced as counterion of the positively charged cetyltrimethylammonium (CTA^+) surfactant that stabilize the plasmonic colloids in suspension. Those three important aspects (Cl^- act as shape directing agent, AgCl insoluble species are formed in solution and CTA^+ moieties of CTA-Cl is important for colloidal stabilization) have been determined in separated studies. Therefore, a challenge relies in decoupling the respective effects to provide a more unified view of the growth processes.

Kinetic studies

Publication relative to this work:³⁴⁻³⁷

supervision: Jieli Lyu (PhD), Kinanti Aliyah (M2), Samantha Roque (M2), Masa Johar (M1)

Collaboration outside LPS: LCTEM : Damien Alloyeau (MPQ, Université de Paris), SAXS : Thomas Bizien (Synchrotron SOLEIL)

Bimetallic particles (BPs) consisting of a gold core covered with a silver shell^{21, 38} are very promising in view of applications, as they allow fine control over the position of the plasmon resonance peaks. Their growth has been monitored over time using UV-Vis-NIR extinction spectroscopy.^{15, 39, 40} This technique is widely available, has excellent time resolution and is very sensitive to the particle morphology, but the position of the plasmon peak cannot be used to directly retrieve particle dimensions in the case of anisotropic nanoparticles; thus, one cannot extract the complete kinetical information using this technique. Small Angle X-Ray Scattering (SAXS) has been extensively used to characterize the growth of homogeneous (single-metal) spherical^{16, 18, 41-43} and anisotropic^{44, 45} nanoparticles but it has been very seldom applied to bimetallic objects, in particular because the data treatment is much more involved in this case. The advantage of SAXS is that it can yields the particle size unambiguously, if the dimension of the NPs does not exceed the q range of the system. Moreover, UV/Vis spectroscopy and SAXS can be used to retrieve the concentration of NPs which is routinely performed for mono-metallic NPs. In a recent work we have shown that

these techniques could also be applied to determine bimetallic NPs concentration and morphology.^{34, 35} In another work, we have used SAXS to describe the formation of a silver shell at the surface of gold nanorods and found that the growth rate was limited by the surfactant bilayer at the NPs surface.³⁶

Given their limited spatial resolution and the necessity to develop models to retrieve the NP morphology, UV/Vis spectroscopy and SAXS provide an indirect and incomplete overview of the nucleation and growth processes implied in wet-chemical synthesis. Over the last few years, Liquid-Cell Transmission Electron Microscopy (LCTEM) has become a leading method for directly visualizing the dynamics of single nanostructures in their formation medium.^{46, 47} An important feature of this technique is that the electron dose rate can be used to control reaction kinetics because NP formation is generally driven by radiolysis processes.^{48, 49} However, exploiting this *in situ* information in high-yield synthesis remains difficult because radiochemical effects are not involved in conventional protocols. Therefore, an important challenge is to reduce the gap between nanoscale *in situ* observations and bench-scale synthesis, by correlating LCTEM results with *in situ* techniques based on light-matter interactions, which probe large NP ensembles without radiolysis effects.

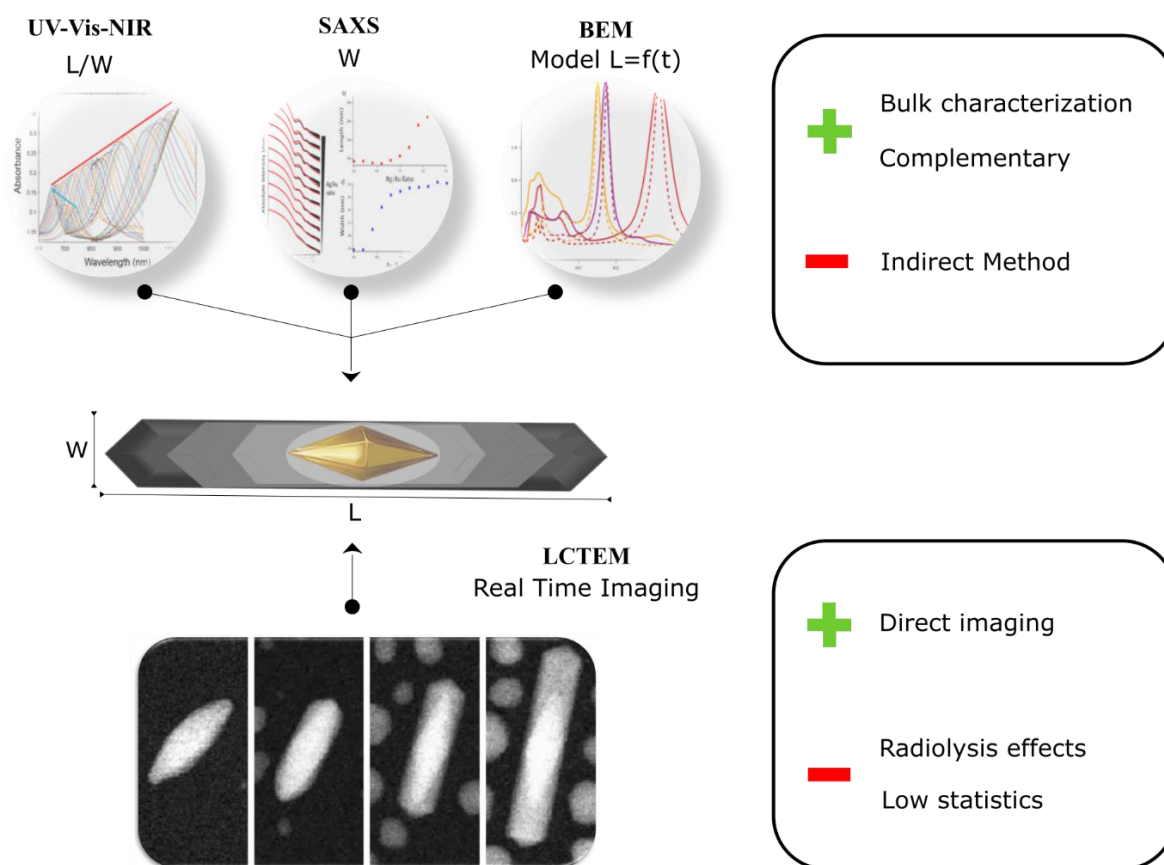


Figure 3-3: Schematic representation of the methodology for the real time investigation of Au@Ag rod growth. A combination of bulk experiment techniques and numerical modelling in conjunction with direct LCTEM imaging is used to follow the reaction.

In this work,³⁷ we studied the growth of silver at the surface of pentatwinned gold bipyramids, ultimately forming silver nanorods (**Figure 3-3**). Interestingly, we noticed no effect of the growth rate on the final shape of the nanoparticles, indicating that the anisotropic growth is governed by thermodynamic effects. We also have shown the key role of AA in guiding silver-on-gold growth process. This was surprising in the first sight since AA is commonly described as a mild-reducing agent, here we demonstrated that it is also a shape-directing agent.

Shape control and symmetry breaking in seed-mediated growth in mixed solvent

Publication relative to this work: ^{50, 51}

Collaboration outside LPS: MD Simulation: Eric Hill (Univeristy of Hamburg, Germany)

Collaboration inside LPS: HRTEM: Marta de Frutos, EELS : Xiaoyan Li, Mathieu Kociak

Dimethyl sulfoxide (DMSO) is completely miscible in water and the micellization of surfactants in such mixtures is strongly modified with respect to pure water.⁵²⁻⁵⁵ [ENREF 27](#) In general, the critical micelle concentration increases with the DMSO content, up to a threshold value above which no micelles form. Since surfactants play a key role in the synthesis of plasmonic NPs,⁵⁶ we hypothesized that supplementing the reaction mixture with DMSO could modify the NPs' morphology. Although DMSO-water mixture have been studied extensively, DMSO has seldom been used in colloidal chemistry.⁵⁷⁻⁵⁹ For instance, it was used as a solvent and shape-directing agent in order to stabilize the {311} facets of Au bipyramids with an octagonal cross section.⁵⁸ In another example, coordination of DMSO to the surface of gold nanorods favored the formation of Au@Ag octahedra.⁵⁹

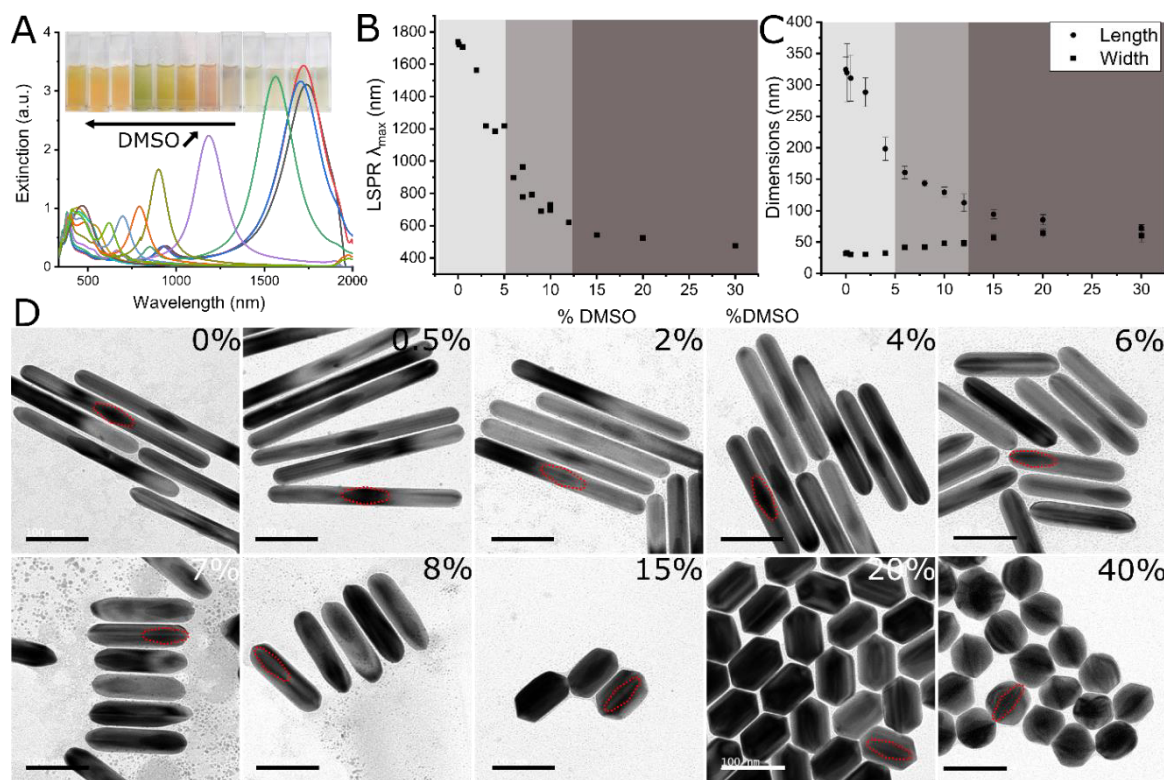


Figure 3-4: Morphological control by tuning DMSO concentration. A) Extinction spectra of Ag rods synthesized with various DMSO concentrations. The inset shows images of the corresponding dispersions in cuvettes. B) Position of the longitudinal surface plasmon resonance (LSPR) as a function of the DMSO concentration. The three grey-shaded areas denote three different morphologies: symmetric rods (left), asymmetric rods (middle), isotropic NPs (right). C) Size dispersion (length and width) obtained from TEM image analysis of Ag rods for different DMSO concentrations. The grey shades denote NP morphologies as in B). D) Representative TEM images of the Ag rods synthesized with varying DMSO concentration. Scale bars on all images are 100 nm.

In this work, a simple, yet robust approach to promote asymmetric growth of Ag on AuBPs was achieved by the addition of DMSO to an aqueous reaction medium. The volume fraction f of DMSO was systematically varied and its influence on the morphology and symmetry of the AgNRs was described. We identified 3 growth regimes: (i) longitudinal symmetric growth (f between 0-4%), (ii) longitudinal asymmetric growth (f between 6-10%) and (iii) transverse symmetric growth (f above 20%) (**Figure 3-4**). Experiments showed that DMSO replaces the capping agent at the NP surface and decreases the Ag deposition rate. In order to better understand the molecular interactions at the gold interface under synthesis conditions, all-atom MD simulations were performed which showed a significant modification of the chemical environment of the Au surface: DMSO strongly binds to the Au(111) interface, displacing interfacial water and reducing its long-range structure, while also reducing the interactions between both Cl^- ions and CTAC micelles with the Au interface. Longitudinal asymmetric growth is induced by DMSO adsorption which influence Ag reduction kinetics

while transverse growth is induced by alteration of the CTAC micelle geometry at high DMSO content. In addition to establishing a simple, colloidal approach for asymmetric AgNR growth, this work gives new perspectives for the study of the physical properties of asymmetric NPs. Furthermore, this work shows the potential of DMSO in controlling the synthesis of complex nanostructures and tailoring their linear and nonlinear optical properties, which will advance applications in multimetallic photocatalysis and chemical sensing, to name a few.

Imparting inorganic lyotropic liquid-crystal with plasmonic properties

Publication relative to this work: ^{60, 61}

PhD student involved: Karin El Rifaii (PhD)

Inorganic lyotropic liquid-crystal (ILC) are intermediate states of matter, in which anisometric inorganic particles (e.g. rods, plates) are ordered in space like a crystal while maintaining fluid properties of a liquid.⁶² A wide variety of anisometric nanomaterials self-organizes spontaneously in LC phases,⁶³ as a result of a gain in packing entropy ruled by excluded-volume interactions.⁶⁴ Research in this fast-growing field is motivated by the accurate control on the organization of individual particles, even at low volume fraction, over periodic distances up to the visible wavelength range and with significant response to external stimuli.⁶⁵⁻⁶⁸ I collaborated recently with Erwan Paineau and Patrick Davidson on these aspects. In these works, we built upon the seminal work of Liz-Marzán and Philipse^{69, 70} and on our experience in the LC phases of clay nanoparticles^{71, 72} to study the self-organization of different NPs/ILCs hybrids. Metallic salts (Au or Ag or Pd or Pt) were then reduced in situ using sodium borohydride without any surfactants or ligands. Interestingly, the NPs are grafted on the inorganic nanoparticles (imogolite nanotube and beidellite nanosheets). The obtained NPs/ILCs hybrids form colored dispersions that display birefringence when imaged between crossed polarizers. This confirms the effective synthesis of stable NPs in the liquid-crystalline host. These colloids display plasmonic structural colours and they can be aligned by an electric field, which is relevant for fundamental and materials chemistry of colloidal LC.

COLLOIDAL SELF-ASSEMBLY INTO ONE DIMENSIONAL CHAINS

Introduction

GNPs are easily assembled into compact structures, e.g. by van der Waals or depletion forces, but it is much more difficult to obtain open or elongated patterns. In this respect, end-to-end assembly of GNPs into long chains (plasmonic polymers) have received much attention from the scientific community since the pioneer work of Kumacheva in 2007.⁷³ Interestingly, there is a marked similarity between the self-assembly of metal nanoparticles and polymerization of organic molecules.⁷⁴ Modelling the optical properties of 1D chains showed that the dominant spectral feature, a strongly scattering super-radiant mode, typically red-shifts upon particle addition until reaching a gap-size-dependent “infinite chain limit” around ten colloidal repeat units.^{75, 76} In comparison, the longitudinal dipolar plasmon mode of a nanorod continuously red shifts upon increasing aspect ratio.⁷⁷⁻⁷⁹ Experimental and theoretical studies have also revealed the great dependence of the extinction cross section of colloidal chains as a function of the interdistance.^{75, 80} Furthermore, the hot-spots formed at the NPs junction provides significant SERS enhancement.⁸¹ Experimental studies are either based on single particles spectroscopy techniques comprising optical (dark field scattering) and electronic (energy electron loss spectroscopy) excitation or ensemble measurement by UV/Vis spectroscopy complemented by ex-situ TEM. In line with the theoretical predictions, the wavelength of the extinction maximum red-shifted with increasing particle number toward a chain-morphology-dependent limit.^{75, 80, 82, 83} Besides tailoring the polarization-dependent scattering and absorption properties, linear nanoparticle arrangements allow plasmonic waveguiding via near-field coupling. Such particle-based waveguides enable energy transport below the diffraction limit without excessive radiation leakage, but the achievable attenuation length depends sensitively on the interparticle distance and choice of the optical guiding mode.⁷⁵ Addressing the dark sub-radiant modes of close-packed, self-assembled nanoparticle chains via asymmetric excitation is highly efficient for plasmonic energy transport over distances of several microns.^{75, 82} Quantum mechanical effects arise in plasmonic structures with subnanometre gaps as well as charge transfer plasmon modes below 0.3 nm distances.⁸⁴ Charge transfer plasmon modes can be tuned by mean of controlling the conductivity of the gap region by varying the distance, with conductive molecular bridges or by melting adjacent particles.

Assembly mediated by sulfate ions and further processing

Publication relative to this work:^{85, 86}

Collaboration outside LPS. LCTEM: Damien Alloyeau (MPQ, University of Paris Cité)

Collaboration inside LPS. EELS: Xiaoyan Li, Mathieu Kociak

supervision: Jieli Lyu (PhD)

Colloidal chains have been obtained by wet chemical approaches,⁸⁷ including but not limited to molecular recognition⁸⁸⁻⁹³ or solvophobic interaction^{73, 74} or mediated by templates.⁷⁹ In many cases, the self-assembly reaction progress until flocculation and can be difficult to handle. In this respect, it is crucial to control the assembly process and stabilize a preferred configuration with defined optical properties. This requires the ability to controllably manipulate the reaction rate that can be achieved by an external actuation. Light-controlled synthetic procedure has been shown but this type of technique necessitates a femtosecond laser tuned to the plasmon frequencies of the nanoparticles.⁹⁴⁻⁹⁶ Benchtop methods relying on chemical actuation have been developed to prevent the growth of larger structures such as a molecular competitor^{94, 97} (e.g. addition of an excess of mono-thiol to compete a dithiolated linker mediated assembly) or by means of encapsulating the oligomers.^{98, 99} In these cases, the surface of the oligomers as well as the interparticles gaps are passivated by strongly bonded ligands that may act as a bottleneck for further uses. In a recent work, Vikesland and coworkers provided an alternative to dithiolated linkers by showing that sulfate ions can mediate end-to-end attachment of gold nanorods.¹⁰⁰ Inspired by this study, we refined the method in the view of finely tuning the assembly kinetics and stabilize the oligomers in suspension (**Figure 4-1**).

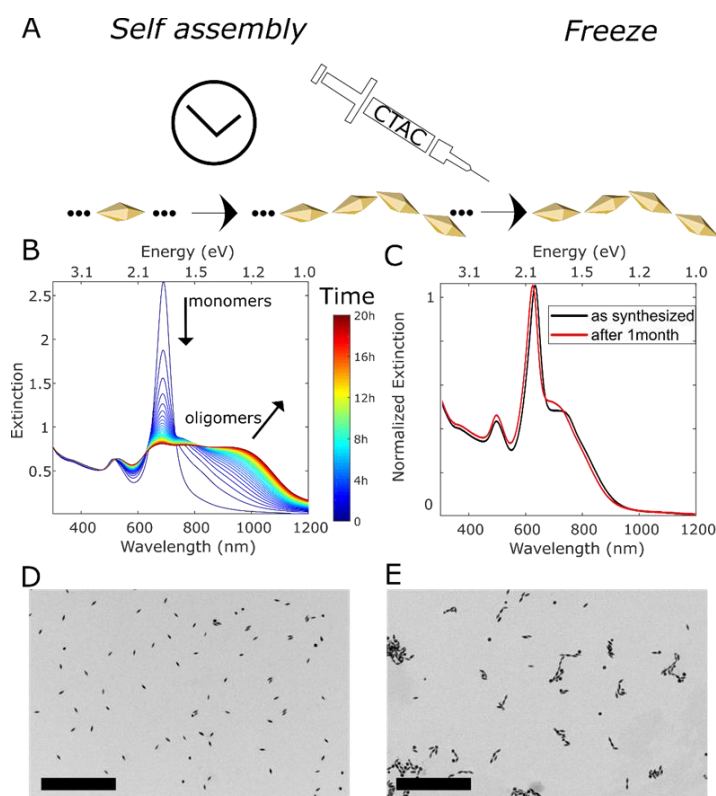


Figure 4-1 : Chain formation and colloidal stabilization. **A)** Scheme illustrating the tip-to-tip assembly of GBPs mediated by sulfate ions and the process used to quench the system by the addition of CTAC. **B)** Series of extinction spectra during the assembly of GBPs mediated by sulfate ions, acquired at time intervals of 30 min. **C)** Normalized UV/Vis spectra of an oligomers suspension immediately after supplementing the solution with CTAC (black line)

and the same dispersions after 1 month (red line). **D-E)** Representative low-magnification TEM images of GBPs (d) before and (e) after assembly (20h of reaction). Scale bar is 500 nm.

We assembled rods, bipyramids and sphere and showed that the process is driven by sulfate ions at a reduced CTAB concentration (a few micromolars). Kinetic investigation by UV/Vis spectroscopy revealed a self-assembly process with an apparent first-order kinetic. Time resolved SAXS analysis at the beginning of the process showed an intermediate stage at which the nanoparticles immediately self-assemble upon dilution with a relatively large interdistance (large enough to not be detected by UV/Vis spectroscopy). This “clustering” step is related to the dilution of the surfactant well below its critical micellar concentration, which lead to the destabilization of the NPs suspension. This finding highlight the importance of using complementary techniques to characterize materials. The organization into chains is then evidenced on longer time scales by the progressive red-shift of the plasmon band (**Figure 4-1**). Our method allows to control the kinetic of the self-assembly process (between minutes to days) by tuning CTAB concentration. Without additional intervention, the reaction progressed until flocculation. Fortunately, we found that the self-assembly process can be stopped at the desired stage simply by adding excess surfactant to the reaction mixture which was convenient for further uses. We hypothesized in the first place that the NPs would have a certain degree of freedom to move within the assemblies and we performed LCTEM on the oligomers to test this hypothesis. We found very little fluctuation within the assemblies, showing that the interaction is extremely directional and quite strong. We also analyzed the degree of polymerization (the number of particles per chains) by *ex situ* TEM by extracting aliquot during self-assembly. We found that the degree of polymerization was well predicted by the Carothers equation. In this sense, the plasmonic polymers seems follows a step growth mechanism (both monomers and oligomers can self-assemble¹⁰¹).

We then took advantage of the stability of the plasmonic oligomers to control the metallurgy of the hotspots by seed mediated growth. In order to build nanojunction, it is important to introduce a relatively low quantity of metal (e.g. 0.2 molar equivalent Metal/Au) to avoid the formation of core-shell structures. Silver, palladium and platinum have been deposited in this way (Figure 4-2). A clear evolution of the optical properties was observed by UV/Vis spectroscopy and by STEM-EELS on individual oligomers. Interestingly, the LSPR was shifted from the visible toward the mid-infrared window after the formation of the junction. Our method is simple, scalable and yields high-aspect ratio nanostructures with tunable optical properties across a wide spectral range.⁸⁶

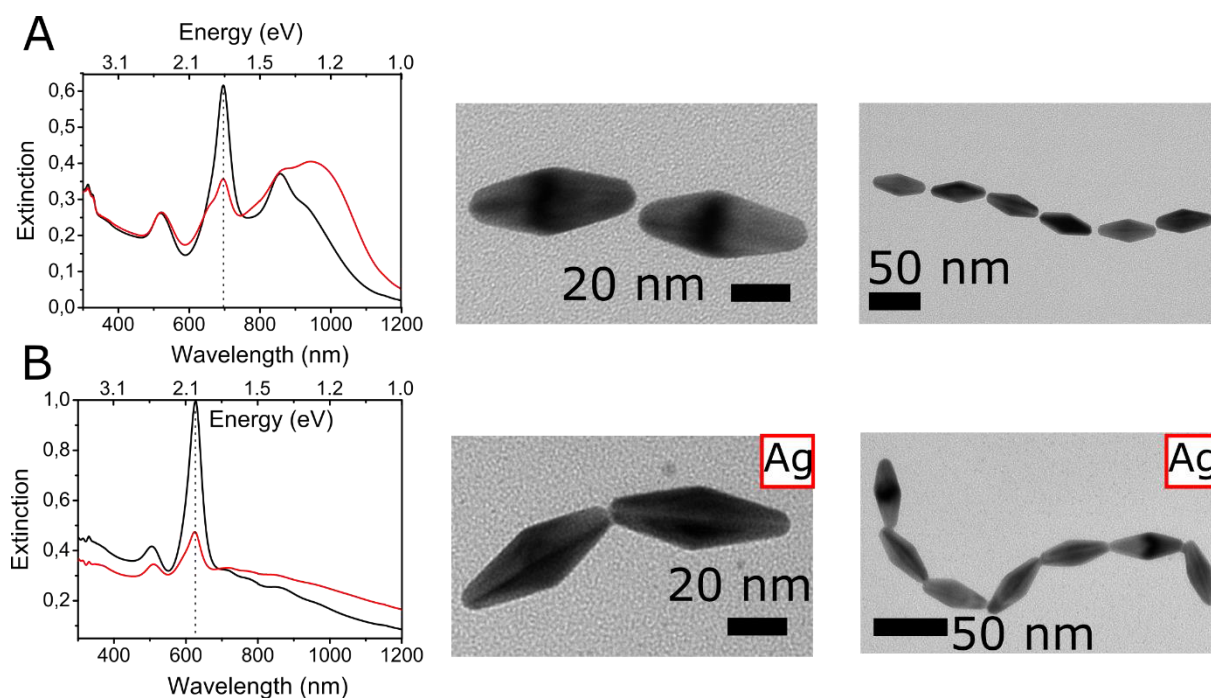


Figure 4-2 : Tunable conductive nanojunctions in plasmonic oligomers engineered by seed-mediated growth. A) UV/Vis spectra of two oligomer suspensions in which the self-assembly process was frozen after 5h and 20h. TEM images of corresponding oligomers. B) UV/Vis spectra and TEM image of oligomers of the same suspensions after growing nanojunctions of silver.

EVAPORATION INDUCED SELF-ASSEMBLY

Introduction

Evaporation induced self-assembly (EISA) techniques are probably among the most studied methods to organize colloidal suspension into an ordered material. Drying leads to a progressive increase of concentration that will eventually induce ordering in the material. These structures are kinetically trapped in non-equilibrium states, meaning that they depend sensitively on the evaporative route taken. Experimentally, slow evaporation rate (e.g. 6h for a 10 μ L sessile drop) are important to observe crystallization and the types of deposit are correlated with the mode of liquid evaporation. For instance, when a sessile drop containing colloids dries on a solid surface, it leaves a dense, ring-like deposit along the perimeter, i.e., forming a “coffee ring” on the surface.^{102, 103} This phenomenon occurs because the contact line is pinned and the liquid evaporating from the edge is replenished by the liquid from the interior, inducing flow carrying the colloids to the droplet periphery. Although different methods can be used to limit this effect (e.g. introducing Marangoni flows, using hydrophobic substrate), it generally affects the macroscopic deposition of the colloids that can be detrimental for potential applications. Moreover, considering the interaction between NPs is also important to design colloidal assemblies and I redirect interested reader to reviews on this later topic.¹⁰⁴⁻¹⁰⁷

Fortunately, the “coffee ring challenge” can be partially overcome. In a pioneering work, Lewis and coworkers used a mask consisting of holes organized in hexagonal arrays to control the accumulation of silica microspheres at the uncovered region, where evaporation was faster than at the covered parts.^{108, 109} The evaporation rate could also be enhanced at the uncovered regions by illumination with an IR lamp.¹¹⁰ A mixture of gold nanoparticles and polymer particles were dried by this method, leading to a periodically organized plasmonic composite.¹¹¹ More recently, a pyramidal mold was used to direct the organization of gold nanospheres into macroscale arrays of plasmonic pyramids.¹¹² In this work, the mold was first filled with the metallic NP, and then assemblies were transferred onto a flat substrate by stamping. Vakarelski et al. demonstrated formation of gold wires in a macroscale connected network using a colloidal mask of latex beads.¹¹³⁻¹¹⁵ Importantly, the addition of surfactant was important to stabilize the liquid film and allow the formation of the plasmonic network upon drying. In order to improve the reproducibility and versatility, the authors used a photoresist as a mask to direct the drying of the gold suspension.¹¹⁶ An alternative method is screen printing, so that the resulting structures could be tuned via the screen mesh.¹¹⁷ Microfluidics is another appealing technique in this field as it allows control over the addition of reactants, easy monitoring of the self-assembly process and versatility over chip design. To overcome the use of expensive syringe pumps and tubing, solvent flow can be induced by capillarity (MIMIC)¹¹⁸⁻¹²⁰ or by microevaporation,¹²¹ rendering these approaches attractive in the field of particle crystallization.

Templated approaches

The work described in this section was initiated during my PhD (supervised by Pascale Even-Hernandez and Valérie Marchi) in which we worked in close collaboration with the *Institut de Physique de Rennes* (Marie Postic, Laurent Courbin and Frank Artzner). During my PhD, a PDMS mold was used to control meniscus morphologies at the gaps between cylindrical posts, which were engineered by soft lithography allowing great versatility on features morphology and spacing.^{122, 123} [ENREF 122](#) We demonstrated a hierarchical organization of gold nanorods into smectic phases. I then joined in post doc the group of Luis Liz Marzan whose research span from the precise synthesis of gold NPs, to their self-assembly and application for sensing applications. I collaborated with Lourdes Basabe Desmont (BIOMICS, UPV/EHU) to get a different PDMS template comprising an array of micron-sized cavities where the gold NPs could be confined in a more precise manner.¹²⁴ The goal was initially to insert the nanoparticles in the cavities but we quickly realized that the nanoparticles deposited on the confining substrate instead. We then pursued research in this direction that is going to be detailed in the next section. This method to obtain plasmonic supercrystal arrays have been further developed and are summarized in **Figure 5-1**.

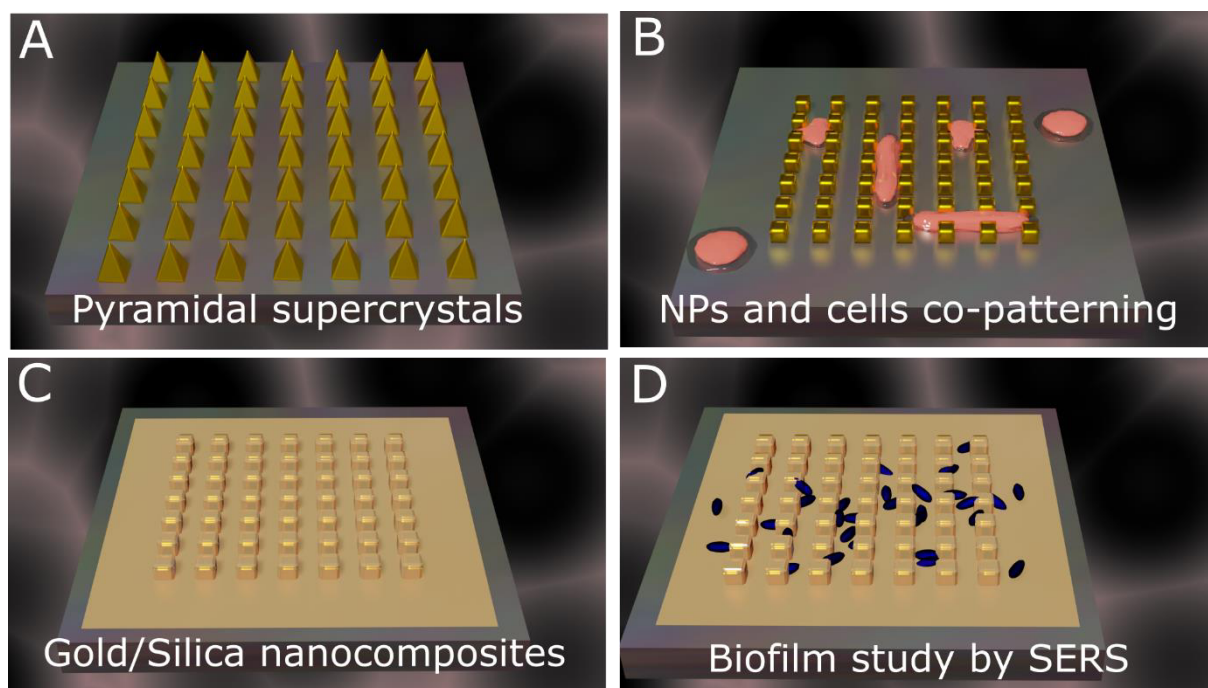


Figure 5-1 : Schematic representation of later development : plasmonic pyramidal arrays (A),¹²⁵ NPs and cells co-patterning (B),¹²⁶ Gold/silica nanocomposites (C),¹²⁷ Detection of quorum sensing in biofilm by SERS (D).¹²⁸

Pyramidal supercrystals. Firstly, we developed the process towards pyramidal supercrystals in collaboration with the group of Lluís F. Marsal (Universitat Rovira I Virgili) whom provided inverted pyramidal templates in silicon substrates.¹²⁵ We prepared the PDMS template by replicating two times the silicon template. Otherwise, the pyramidal supercrystals were obtained by the same approach as previously described. Research on this topic was

motivated by the possible accumulation of an electric near field at the apex of the pyramid that would increase SERS performance. Although a few reports in the literature mentioned this collective effect,^{112, 129} we were not able to reproduce those measurements presumably due to surface contamination with PDMS monomers on the supercrystal surface. On the other hand, we successfully obtained large-scale organization of the NPs.

NPs and cell co-patterning. Secondly, cell adhesion proteins (fibronectin) was deposited on a substrate by microcontact printing together with the NPs, resulting in adjacent patterns of bioactive and plasmonic patches (**Figure 5-1B**).¹²⁶ In this work, we used microfluidic channels as well as micron sized cavities in order to tune the confinement of the NPs and control their self-organization. We also explored the opportunity of seeding cells that were conforming to the shape of the bioactive pattern. Interestingly, cells in contact with the NPs were remotely detached from the substrate by a laser irradiation due to local heating from the NPs. This work was performed in close collaboration with Lourdes Basabe Desmonts (BIOMICS, UPV/EHU) whom provided the templates and Malou Henriksen-Lacey (now research associate in CIC Biomagune) for the cell study. We explored the opportunity of performing SERS *in vitro* but the low measured signals were presumably due to surface biofouling by contaminants from the cell culture media.

Gold/silica composites. In parallel of those research activities, we developed a method to functionalize the supercrystal surface by a mesoporous silica film that would allow percolation of molecules smaller than the pore size and avoid biofouling (**Figure 5-1C**).¹²⁷ This work was performed in close collaboration with Marta Norah Sanz-Ortiz whom was developing such strategy at the single particle level.¹³⁰ To our advantage, silica was found not only to cover the supercrystals but also to infiltrate between gold nanorod layers, thereby increasing the interlamellar distance without drastically affecting the internal organization of each monolayer. This work was performed in close collaboration with Evgeny Modin and Andrey Chuvilin (CIC Nanogune) whom revealed this unexpected deposition of mesoporous silica film inside the supercrystal. The impregnation procedure we developed allowed molecular diffusion in the supercrystal interior that improved SERS performance by almost an order of magnitude.

Biofilm study by SERS. This system was ultimately designed for real time sensing of Quorum Sensing molecules (QS, small diffusible signals secreted by bacteria) in a living bacteria colony (**Figure 5-1D**).¹²⁸ We focused on biofilms of *Pseudomonas aeruginosa*, as these bacteria are one of the leading causes of nosocomial infections in hospitals. Furthermore, the precise biochemical mechanism involved in the development of such biofilms is still a grey box, particularly for the earlier stages of the process because available techniques for the analysis of QS are either based on invasive approaches by means of genetically modified bacteria or non-invasive but in its planktonic form (i.e. no biofilm). Fortunately, the SERS substrate we developed could detect the secretion of QS after only 1h of bacteria seeding (before the biofilm formation) that hold promise for biofilm diagnostic and fundamental studies. Biofilm study by SERS was performed at the laboratory by Eric H. Hill (now group leader in Hamburg University of Technology). This work was one of the

objective of the ERC Advanced grant of Luis Liz Marzan and was performed in close collaboration with the Colloid Chemistry Group in the University of Vigo.

Millimeter size supercrystals of gold octahedra

Publication relative to this work: ¹³¹

Collaboration outside LPS : Synthesis and self-assembly of the gold octahedra, design of the microfluidic chip: Colloid Chemistry group (University of Vigo, Spain). Daniel García-Lojo, Sergio Gómez-Graña, Isabel Pastoriza-Santos, Jorge Pérez-Juste

3D FIB-SEM Tomography: Evgeny Modin and Andrey Chuvilin (CIC Nanogune, Spain)

In this work, we analyze the organization of gold octahedra into single-domain supercrystals obtained by pervaporation within a microfluidic channel that spans millimeters. We use SAXS to investigate the orientation of the supercrystals over large scales and FIB-SEM tomography for local structural characterization in the real space. Interestingly, time-resolved SAXS revealed the crystallization dynamics of gold octahedra *in situ*. The results show single-domain supercrystals extending over the dimensions of the microfluidic channel (millimeters) that were oriented in a reproducible manner from sample to sample. In this work, our experimental contribution at LPS was limited to the structural characterization by SAXS.

The organization into extended superlattices of four octahedra batches (edge length from 52 to 85 nm) was conducted by pervaporation using a microfluidic device. As shown in **Figure 5-2**, a concentrated dispersion of Au octahedra is pumped through the reservoir into a microchannel with a rectangular cross-section of 300 μm width, 25 μm height and around 6 mm in length.

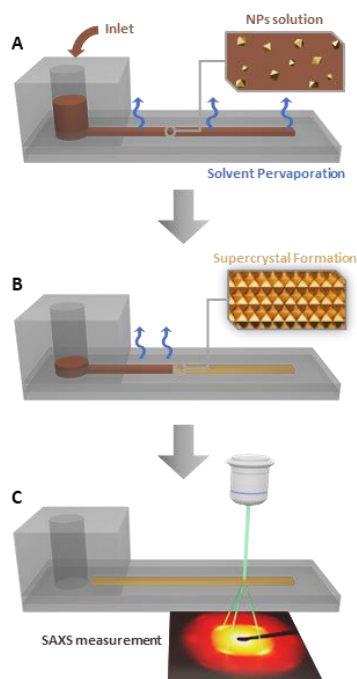


Figure 5-2: Schematic representation of the preparation process of the Au supercrystal by pervaporation. (A) A concentrated dispersion of Au octahedra is pumped within the microchannel and the solvent is allowed to evaporate through the thin PDMS membrane (pervaporation). **(B)** The pervaporation induces the accumulation of the Au octahedra at the end of the microchannel inducing their crystallization and consequently the formation of a supercrystal. **(C)** *In situ* characterization by SAXS during the formation process of the Au supercrystals.

The solvent is allowed to evaporate through the thin PDMS films for at least 6 h. After complete solvent evaporation, the resulting supercrystals were first analyzed in house by SAXS *in situ* across the thin PDMS membrane. Regardless of the edge length of the octahedra, the assemblies exhibited discrete Bragg spots, indicating the presence of a single superlattice spanning areas larger than the footprint of the X-ray beam ($300 \times 500 \mu\text{m}^2$). We next performed *in situ* SAXS analysis on the SWING beamline of the SOLEIL synchrotron along the channel to determine the extension of the supercrystal (**Figure 5-3**). SAXS analysis of the self-assembly of gold octahedra by pervaporation in a microfluidic channel revealed the formation of single-domain supercrystals. To the best of our knowledge, the size of the supercrystals is among the largest reported to date for plasmonic NPs ($1.7 \times 0.3 \text{ mm}^2$). Supercrystal analysis by SAXS and FIB-SEM tomography indicated the formation of extended superlattices with a monoclinic $C/2m$ crystalline symmetry. Supercrystal formation was also investigated by time-resolved *in situ* SAXS, revealing a multistep formation process, with a first accumulation stage when the nanoparticles concentrated in the channel, followed by nucleation and crystal growth. Moreover, we found that the orientation of the supercrystal did not change during the growth, leading to a single-domain supercrystal, which ultimately adopts the shape of the microfluidic channel. This pervaporation approach favored the formation of the monoclinic lattice at the expense of the other polymorphs usually observed by other EISA approaches. Therefore, we demonstrate that the self-assembly process leads to the formation of large single-domain supercrystals with potential plasmonics and optics applications for analytical chemistry.

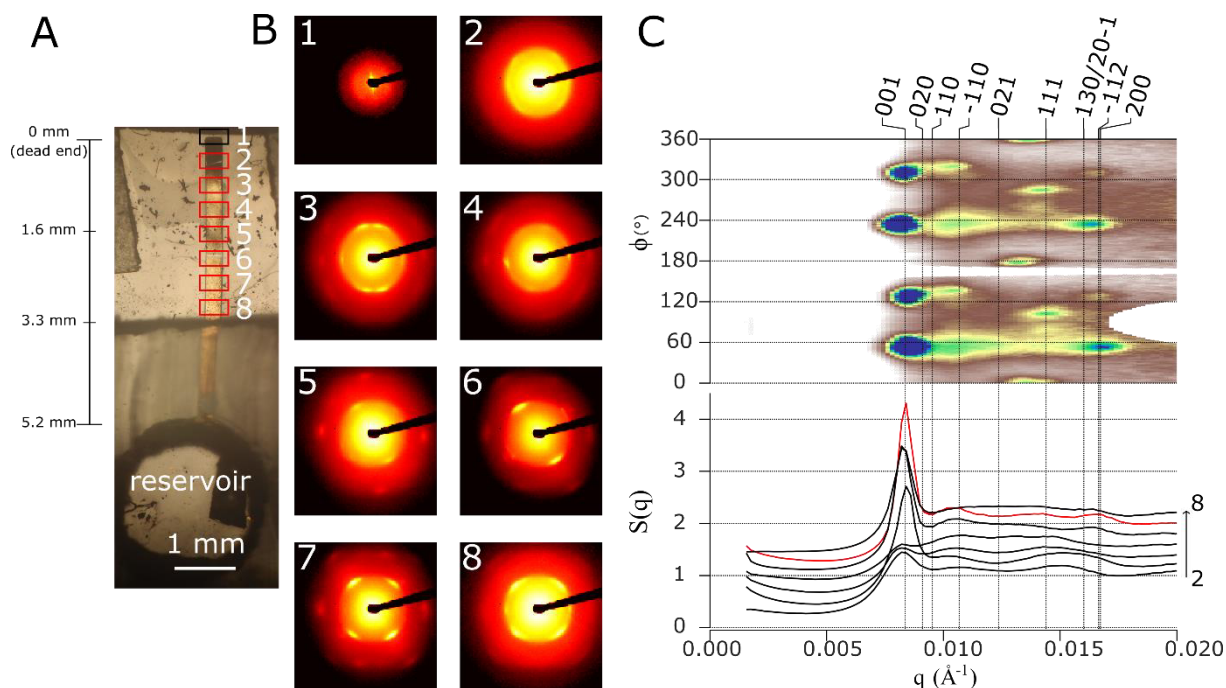


Figure 5-3: In-situ space-resolved SAXS analysis of the gold octahedra supercrystal. (A) Optical microscopy image of the microfluidic chip after formation of the octahedra supercrystal. (B) Two-dimensional SAXS images acquired at different zones of the channel, indicated in (A) with numbered rectangles. The dimension of the rectangles corresponds to the footprint of the X-Ray beam ($300 \times 500 \mu\text{m}^2$). SAXS images are shown on a logarithmic intensity scale. (C) (top) Image representing the angular distributions of the Bragg peaks on position 7 and (bottom) structure factors of supercrystals obtained from position 2 to 8. Vertical lines indicate the expected positions of the Bragg peaks for the C/2m monoclinic space group. Measurements performed on Oh₈₅ at SWING.

Shaping supercrystals by nesting shapes

Publication relative to this work: in preparation

Collaboration outside LPS : SAXS Thomas Bizien (SWING beamline, Soleil) and Doru Constantin (ICS, Strasbourg)

supervision: Jieli Lyu (PhD), Wajdi Chaâbani (post-doc)

Nature has long inspired scientists with its ability to synthesize complex inorganic nanostructures by consistently exploiting the self-assembly in confinement of (often complex) building blocks. This level of complexity has not yet been reached synthetically with colloidal crystals, because most nanoparticles (NPs) are highly symmetric objects and because their self-assembly is unconstrained. In order to overcome this limitation, the NPs' shape and environment should be tuned to "frustrate" crystallization.¹³²⁻¹³⁴ These strategies are appealing to obtain arrangement of particles with a lower symmetry than standard approaches that is

relevant for metamaterials architecture design. Aspects of self-assembly in confinement¹³⁵⁻¹³⁸ and shape-directed assembly^{104, 139-143} have been studied separately, but very seldom while acting together.^{68, 144-148} Most of the studies combined encapsulation of the colloids within emulsions droplets and evaporation induced self-assembly (EISA) or Ostwald ripening for assembling the colloids. Although this so-called spherical confinement could be tuned in some extent by controlling the initial volume fraction of the colloids in the droplets, Laplace pressure do not allow tuning the confinement geometry. Control of the crystal habit result in faceted supercrystals, which are typically obtained under thermodynamic control.¹⁴⁹⁻¹⁵² We hypothesized to have a handle on NPs crystallization by imposing boundary conditions for the assembly of the supercrystal for controlling NPs orientation and defect formation.

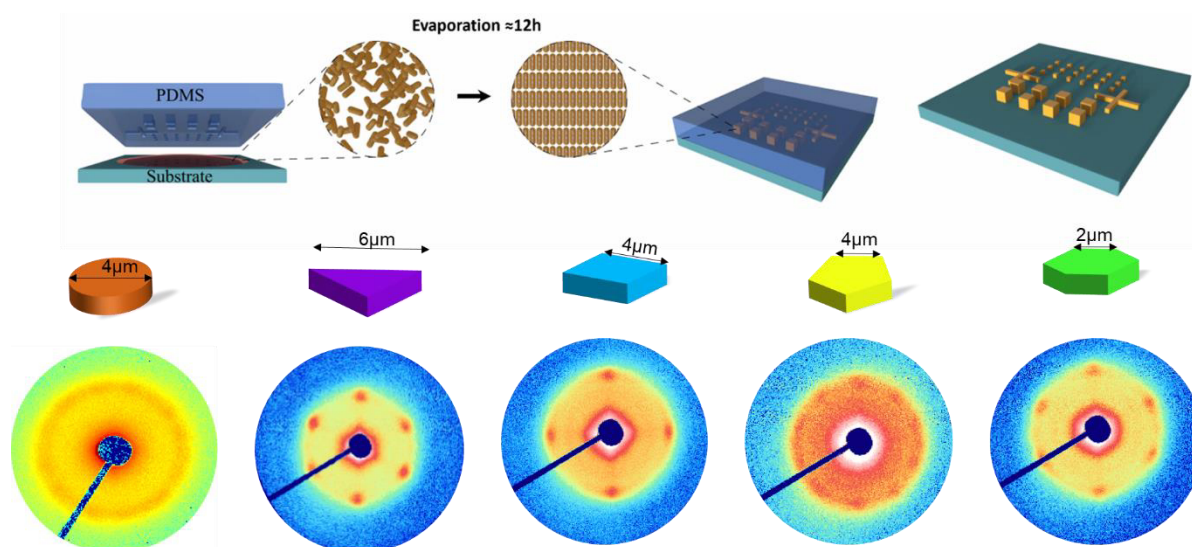


Figure 5-4: Description of the method and the cavities morphology. Bottom: 2D SAXS images acquired at different zones of sample consisting of supercrystal with different polygonal cross-section.

SAXS have been performed at LPS and at SOLEIL. Since the beam footprint spans hundreds of micrometers, the characterization is averaged over many supercrystals. Remarkably, the 2D SAXS images show a discrete number of Bragg spots depending on the supercrystal shape. SAXS image analysis (not shown) shows that the structure of the supercrystal is the same across the different shapes. However, the supercrystals are polycrystalline with monodomains having preferential orientation. We correlated these observations with SEM image analysis and μ SAXS at the SOLEIL synchrotron, in which FFT of single supercrystal could be directly compared with one μ SAXS image of the same supercrystal. The detailed structural analysis shows that such template approaches can control topological defects formation at the grain boundaries, which is promising for future studies (see perspectives).

Crystallization of NPs with pentagonal cross-section

Publication relative to this work: ¹⁴²

Collaboration inside LPS : Computer simulation: Frank Smallenburg

Collaboration outside LPS : 3D FIB-SEM Tomography: Evgeny Modin and Andrey Chuvilin (CIC Nanogune, Spain). SAXS (SOLEIL): Thomas Bizien and Doru Constantin (ICS, Strasbourg).

supervision: Jieli Lyu (PhD), Jules Marcone (PhD), Wajdi Chaâbani (post-doc)

Covering the plane with regular shapes is a complex and intriguing question that has seen sustained interest since antiquity. Among them, regular pentagons are special because unlike triangles, squares and hexagons, they do not tile the plane without gaps. This made them attractive for use in decorative patterns, such as the traditional Chinese ice-ray motif inspired by the growth of ice crystals into ‘rays’, which is a periodic striped phase consisting of alternate rows of pentagons in two different orientations.¹⁵³ European scientists, philosophers and artists, such as Albrecht Dürer or Johannes Kepler,¹⁵⁴ also studied regular arrangements of pentagons, like the so-called Dürer packing. Hales and Kusner have recently demonstrated that the ice-ray configuration has the largest possible packing fraction (0.921) by a computer assisted proof.¹⁵⁵ Ice-ray packing was first demonstrated in numerical simulations in 2005, by the group of Frenkel.¹⁵⁶ At lower packing fraction a rotator/plastic phase was found, in which the orientational order for the pentagons was lost while the positional order adopted a hexagonal arrangement. Mathematicians have predicted the existence of other crystalline polymorphs with a slightly lower packing fraction, but these lattice polymorphs have yet to be encountered in experiments. Two works have been carried on this topic using either pentagonal gold bipyramids or pentagonal silver nanorods as building blocks.

Double lattice packing of gold bipyramids

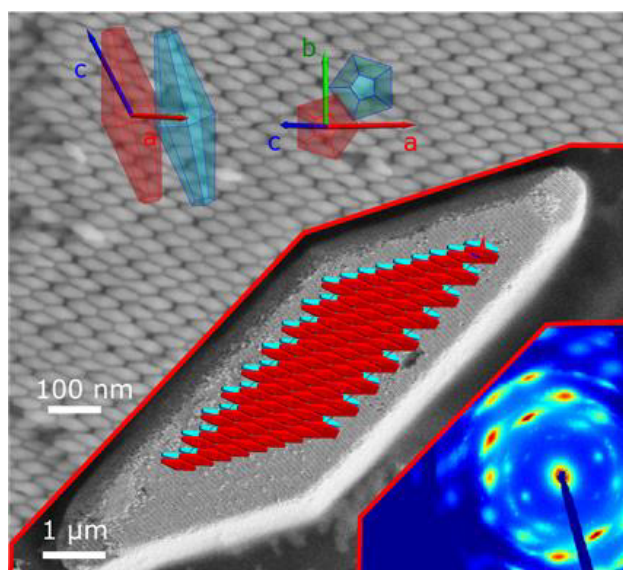


Figure 5-5. Table of content of this work: Pentagonal gold bipyramids are organized into extended superlattices by evaporation-induced self-assembly. SAXS and FIB-SEM tomography analysis indicated the formation of supercrystals with a low symmetry triclinic structure and with a two-particle unit cell. Monte Carlo simulations confirm that the structure corresponds to the densest possible packing. The supercrystals display a facet-dependent optical response that is promising for sensing, metamaterials applications and for fundamental studies of self-assembly

processes.

This work shows that fivefold symmetry and anisotropy can be combined to crystallize complex nano-objects into triclinic pinacoidal supercrystals. Pentagonal gold bipyramids pack into crystals with two particles per unit cell, corresponding to the densest packing predicted by Monte Carlo (MC) computer simulations. Further simulations show how the cross section influences the arrangement (symmetry and packing fraction) of the particles, beyond pentagonal bipyramids. Objects with an odd-sided base are non-centrosymmetric but the two-particle unit cell retrieves inversion symmetry, explaining the double-lattice arrangement. Surprisingly, their packing fraction is lower than that of even-sided particles. The double-lattice packing generalizes the optimal packing of regular pentagons in the plane, the ‘pentagonal ice ray’ in a non-trivial manner, since the section of the bipyramids is not constant along their long axis. This gold bipyramid supercrystal has a facet-dependent optical response, with spiky and smooth facets displaying respectively high and low SERS efficiency. Its low-symmetry triclinic structure is also useful for metamaterials applications and for fundamental studies of self-assembly processes. In this work, we did not observe the ice-ray packing in the real space. We thought about self-assembling pentagonal nanorods because their section is constant along the symmetry axis and therefore their packing could eventually be described in 2D, which would simplify the structural characterization (see next work).

Silver nanorods/nanoprisms

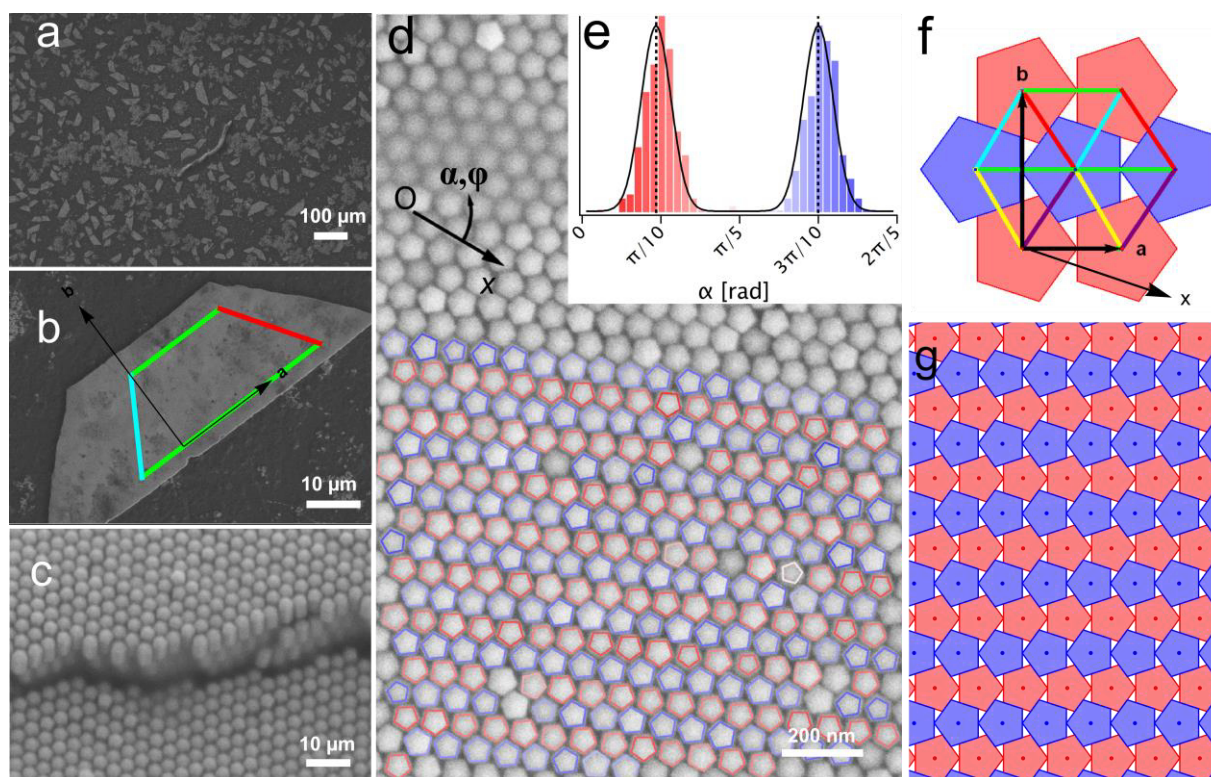


Figure 5-6 : Supercrystals with ice-ray packing. (a-b) SEM images of trapezoidal SCs at different magnifications. (c) Side view showing the 2D packing of the nanoprisms at the

surface of the SCs. (d) Close view of an SC surface. (e) Histogram of the orientation angle α for the pentagonal cross-section in (d), with the same color code, and Gaussian fits (solid line). (f) Ice-ray packing annotated with color-coded Delaunay triangles (each color stands for one distance) as well as vectors a and b of the rectangular unit cell. (g) 2D ice-ray packing of regular pentagons. The blue and red colors indicate the two pentagon orientations.

So far, only a few examples of the ice-ray pentagonal packing were already encountered either at the macroscale or at the molecular/atomic scale. Here we obtain a first experimental realisation at the mesoscale with silver nanoprisms self-assembled into extended micronsized supercrystals (**Figure 5-6**). In contrast with plastic/rotator phases, the NPs display high positional and orientational ordering related by a $\pi/5$ rotation. Extended crystalline order is present and its symmetry is not hexagonal but rectangular, which is a clear signature of the ice-ray pentagonal packing. The trapezoidal shape of the SCs is related to the symmetry of the unit cell (via its Delaunay triangles), confirming both the very long-range order of the lattices (extending over hundreds of particle rows) and, indirectly, the excellent size and shape monodispersity of the samples. The presence of polymorphs for crystalline pentagonal packing gives rise to a rich phase behavior. Along with the ice-ray packing, other crystalline structures are evidenced, like the Dürer packing and intermediate polymorphs. Crystal twinning was also observed. Our analysis reveals a subtle interplay between orientational and positional order. On the one hand, pentagon orientation is conserved even across the boundary between two twin ice-ray crystals or between two types of packing (e.g. ice-ray and Dürer). On the other hand, as the particle's width gets smaller, orientational order decreases while the positional one, given by the length and orientation of the bonds between neighboring NPs, remains fairly constant. Thus, the lattice persists even as the disorientation increases, supporting the presence of the rotator phase detected in numerical simulations.¹⁵⁶ The presence of polymorphs can be rationalized by a compromise between the structure that reach the densest packing (i.e. ice-ray) and the structure that maximise face to face contact (i.e. Dürer). Although the Dürer structure is less dense than the ice-ray, it allows the formation of face-to-face interparticle contacts, which are favored by strong and localized interactions such as the Van der Waals attraction. This result in the formation of many lattice polymorphs that can be describe by the continuous sliding transformation between the two structures. In this sense, the nanoprisms we study in this work are different from other polyhedral nanocrystals such as octahedra, which assemble in a few lattices polymorphs.

RESEARCHES PERSPECTIVES

Synthesis

Improving size dispersion and shape control trough kinetic studies

In a similar way than two snowflakes are different, two gold nanoparticles from the same batch are distinct from each other. State of the art size distribution of anisotropic gold nanoparticles is about 10% and can be pushed to 5% in some cases. Can we go further or did we reach an intrinsic limitation of seed mediated growth? There is probably other chemicals to use or combine to optimize the synthesis of nanoparticles (shape and monodispersity). One recent advance reported herein was the use of a co-solvent (DMSO) modifying the micellization of surfactant in order to control the shape of AgNRs. In the future, modifying the structure of the soft corona during synthesis will be an appealing strategy toward new nanostructures, as shown by other recent studies.^{157, 158}

Heterogeneity in nanoparticle synthesis can rise from thermal fluctuation and improper mixing. In this sense, programmable chemistry combined (or not) with fluidic technologies is already a path under exploration to overcome such limitations. For instance, reducing the dimension of the system in microtubes decrease thermal fluctuation. Interestingly, synthesis in such device can be monitored at a high temporal resolution (milliseconds) by in situ SAXS in order to study fast process such as nucleation. The opportunity to control precisely the injection time is also a way to improve reproducibility, which is often poor between two different persons from the same laboratory. Furthermore, it open the way toward controlled synthesis kinetics that can eventually yield to different product by simply controlling the injection rate. I started in 2023 the supervision of a post-doc (Rahul Nag) to synthesize NPs by programmable chemistry. We will explore how the reaction kinetics influence the NPs shape and monitor the reaction kinetics by UV-Vis spectroscopy.

New twist: In the context of self-assembly, the monodispersity of nanoparticles is most of the time claimed as a fundamental parameter to obtain colloidal crystals. However, mixing particles with two different size ratio can also lead to highly ordered structure (the so-called binary superlattice). This show that playing with size distribution can lead to complex structure. Although attractive for some applications, monodispersity is not the only direction to explore.

Synthesis of new shapes

Synthesis of Janus NPs

Janus NPs have two or more distinct sides with different surface features (shape, composition, and functionalization) and enables the combination of functional properties. The initial aim of the work with DMSO was to produce asymmetric gold/silver NPs, which will be studied in more details in the future. I am envisioning an application for the design of active NPs, which

could convert a chemical fuel into motion. Such nanomotors are usually prepared by a yield-limited step that involve sputtering a catalyst onto a NP layer. Herein, one could take advantage of the higher chemical reactivity of silver to deposit platinum by galvanic replacement, while leaving the gold side without modification. This would be appealing for scaling up the production of plasmonic nanomotors. A short-term solution would be to etch the silver cap on the bipyramids to obtain asymmetric Au@AgNRs. The final aim would be to achieve dissipative colloidal self-assembly in presence of a chemical fuel. Could we observe “plasmonic swarms” of NPs with plasmonic coupling? Could the nanomotors display chemotaxis and migrate in a gradient of chemical fuel? Will the nanomotors be SERS active? How run and tumble motion can be controlled with the aspect ratio of the nanomotors? These questions provide a wealth of research prospect.

Non centrosymmetric nanoparticles for non linear optics and self-assembly

Since gold is centrosymmetric, the second harmonic generation (SHG) response vanishes under homogeneous excitation and the SHG is then due to the particle shape (provided it is non-centrosymmetric itself), to surface defects –notably due to coatings– and, for NPs large enough with respect to the wavelength, to retardation contributions or to the presence of a substrate, which breaks the inversion symmetry. Separating these various effects is a challenge and requires the use of NPs with well-controlled morphology and low surface roughness. Some AuNPs display non-centrosymmetry (asymmetric Au@Ag nanorods, tetrapods, tetrahedra). We recently published the use of gold nanotetrapods for SHG and showed a 10 folds increase of the SHG signal between a tetrapod and a sphere of the same volume.¹⁵⁹ In this context, the ANR MetaTRAP project, led by Pierre François Brevet (Lyon), started in 10/2022. The consortium gathers also Doru Constantin (now at ICS, Strasbourg) and myself for the LPS. We will continue exploring how such NPs can be used for nonlinear optics. Apart from optical application, the tetrahedral NPs are interesting building blocks for self-assembly, displaying structural diversity^{143, 160} and are good candidates to obtain a supercrystal with a diamond structure.

Self-assembly

Self-assembly of faceted NPs

In this document, two works were presented about the self-assembly of NPs featuring a five-fold axis of symmetry (C5NPs). New structures with low symmetry were evidenced. Among the accessible C5NPs shapes, Jieli assembled decahedra as shown by SAXS but the structure still needs to be analyzed. In the case of the pentagonal nanoprism, lattices polymorphs were evidenced presumably because of a compromise between the structure that reach the densest packing (i.e. ice-ray) and the structure that maximise face-to-face contact (i.e. Dürer). We will explore how surface functionalization can be used to stabilize the Dürer packing. We expect to achieve this goal by decreasing repulsion between NPs (uncharged ligands, shorter ligands) to enhance face-to-face contact. Surface functionalization is a

promising way to stabilize structure that is more open by enhancing soft-interaction between NPs. On the long term, the Penrose Pentagon Boat Star quasicrystal packing of pentagons, which is derived from the Dürer packing, is targeted. In a more general way, I am looking for exotic shapes that can be self-assembled. A current trend is the design of chiral NPs, which still features surface irregularities (at this moment unlikely to form supercrystal). Such type of building blocks would be interesting to prepare chiral supercrystal, which could display chirality in their structure at different length scales.

Beyond crystalline structure

The Holy Grail have been for long the obtention of crystalline structure. In my research, supercrystals of low symmetry were obtained by NPs shape design. We already reached the triclinic symmetry using gold bipyramids as building blocks, which is the lowest symmetry among the Bravais lattices. The next direction will be to break further the symmetry of the assemblies by realizing quasiperiodic ordering or introducing defects. Quasiperiodic ordering may be achieved in binary superlattices,¹⁶¹ and more research is needed to such structures with one NP tile.¹⁶² Else, a good way to introduce defects is the templated approach presented in page 32. Preliminary experiment shows that the domains are responsive to light polarization, which is promising to do polarized SERS experiments. This also call for the depth comprehension of the collective plasmonic properties in such systems. Depending on the application, it is not always suited to have physical properties that depends on the orientation of the material. For instance, the elastic properties of commercial materials are often characterized by bulk modulus. In this context, amorphous materials can be described by their degree of hyperuniformity which are ultimately being statistically isotropic with no Bragg peaks like liquids or glasses. Such materials can be interesting for designing materials with collective properties like an isotropic photonic bandgaps (in a material with no translational order!).¹⁶³ Can we achieve hyperuniformity in plasmonic colloidal assemblies? While this is a long-term goal, finding ways to control positional and orientational ordering in colloidal superlattice (so called rotator phase or else plastic crystals) will be explored in more details in the near future.

Emerging techniques for hierarchical organization

Laser driven bubble printing is another method to control the deposition of NPs. A close collaborator, Eric Hill (Hamburg University, Germany), built a microscope to realize such experiments.¹⁶⁴ A focused laser beam is directed onto a substrate (usually plasmonic), and the resulting plasmon-enhanced heating creates a microbubble at the interface between the substrate and the colloidal suspension due to water vaporization.¹⁶⁶ Then, convective flow caused by the temperature gradient drags the colloidal particles down to the substrate. We have shown that colloidal plasmonic NPs could generate such micro-bubble, in order to print the NPs on arbitrary substrates.¹⁶⁴ This open ways to design substrates with controlled topographies, composition and optical activity.

Acoustic levitation is a unique opportunity to address the multi-scale challenges in the field. We will avoid the use of a substrate by performing self-assembly in levitation (overcome the so called coffee ring effect). The progressive evaporation of the solvent will induce phase transitions such as isotropic to (chiral) nematic at certain volume fraction and a macroscopic rearrangement due to 3D confinement. Spherical confinement during the evaporation of the solvent is expected to induce a compromised arrangement, in a similar way that was demonstrated in microfluidics. Interestingly, the system allows tuning the shape of the drop from a sphere to an ovoid as a function of the applied voltage.¹⁶⁵ Herein, acoustic levitation will be used as a new way to study self-assembly in tunable 3D confinement. We will integrate the acoustic levitator on the SWING beamline in order to study self-assembly in real time. This analysis will be correlated with the volume and shape of the drop to reveal the important timestamps in the formation of the material. A post doc (Claire Hotton), co-supervised by Erwan Paineau, will work on these aspects from 2023.

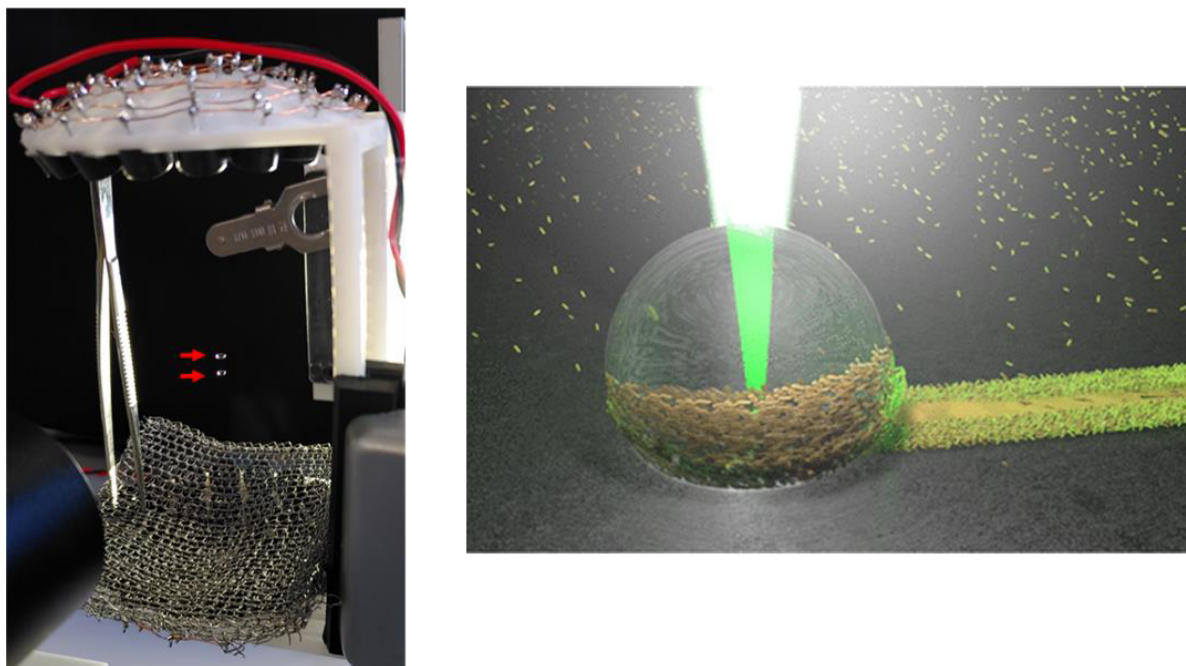


Figure 0-1 : Emerging techniques for hierarchical ordering. Left: acoustic levitation. Right: laser driven bubble printing.¹⁶⁴

Depletion interaction

One overlooked parameter in my research so far is the influence of depletion forces over the assembly of the NPs by EISA. Although the concentration of surfactant is relatively low (a few times the CMC) in the sessile droplet, it progressively increase upon solvent evaporation. In the works described pages 30-33, we empirically found that the NPs could form

supercrystals from a CTAC concentration of 2.5 mM but that no organization was found for lower concentration. This calls for a deeper investigation of such effects.

Depletion forces can be used to induce the self-assembly of nanoparticles in a reversible manner.¹⁶⁷⁻¹⁶⁹ In general, surfactant micelles induce NP flocculation by depletion interaction. Since this process lead to an overall increase of the entropy of the system by excluded volume interaction, it is alternatively denoted as entropy driven self-assembly.¹⁷⁰ The amplitude of this attraction is proportional to the concentration and radius of surfactant micelles and to the area of interaction between two particles. By this process, NPs featuring a high area of interaction form superstructures that sediment to the bottom of the flask, while the smaller NPs remain in suspension. The process is reversible and the NPs can then be redispersed upon dilution. Depletion induced self-assembly has been used to separate plasmonic NPs of different shapes,¹⁷¹⁻¹⁷³ or supercrystals^{131, 140, 142, 174} (when combined with controlled evaporation) but very little for its ability to shape colloidal superlattices.¹⁷⁵⁻¹⁷⁸ Experiments are currently being performed to measure in situ NPs nucleation and growth at high [CTAC]. The next step will be to endow the assemblies with a structural response over specific external stimuli. Since depletion interaction are sensible to the surfactant concentration and temperature, we will naturally explore this opportunity. Another interesting perspective is to use photosensitive surfactant as depletant to assemble/disassemble the NPs under light excitation.

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