ABSTRACTS

-

ORAL PRESENTATIONS

SESSION 4. Nanoparticles synthesis and self-assembly

S4 O1
Jessi VAN DER HOEVEN, Utrecht University, Debye institute for Nanomaterials Science
Self-assembly of gold nanorods in ordered spherical supraparticles

S4 O2
Emilie POUGET, CNRS / Bordeaux University
Chiral gold nanoparticle superstructures directed by silica nanohelices: towards innovative chiroptical properties

S4 O3
Guillaume VIAU, INSA
Ultrathin gold nanowires: growth mechanism and self-assembly

S4 O4
Florian SCHULZ, University of Hamburg
Self-Assembly of Polymer-Coated Gold Nanoparticles

S4 O5
Cyrille HAMON, Laboratoire de Physique des Solides
Colloidal Design of Hierarchical Plasmonic Nanostructures

S4 O6
Takeshi KAWAI, Tokyo University of Science
Ultrathin Gold Films with High Flexibility Prepared by Irradiation with UV Light on Au NPs Monolayer

S4 O7
Susumu KUWABATA, Osaka University
Ionic Liquid-Sputtering Method to Prepare Au Nanoparticles with Some Configurations

S4 O8
Elie NADAL, LPCNO - INSA
In situ synthesis of plasmonic nanoparticles in polymer thin films under laser and solar irradiation

S4 O9
Mai Thanh NGUYEN, Facutly of Engineering, Hokkaido University
Double-Target Sputtering for Au Containing Alloy Nanoparticles

S4 O10
Minna PATANEN, University of Oulu
Surface Chemistry Of Colloidal Surfactant-Free Gold Nanoparticles Generated By Laser Ablation

S4 O11
Valérie CAPS, ICPEES (CNRS UMR 7515, University of Strasbourg)
Insertion of gold nanoparticles within bulk graphite based on peculiar hydrophobic interactions

S4 O12
Angela Federica DE FAZIO, University of Southampton
Light-induced response in DNA-nanoparticle crystals

S4 O13
Richard WEICHELT, Technische Univeristät Dresden
DNA-origami mediated self-assembly of nanoelectronic circuits

S4 O14
Nathalie BRIDONNEAU, Université Paris 7 Diderot UMR 7057 CNRS Laboratoire MSC et Laboratoire ITODYS
Nanostructured inks based on gold nanoparticles and polyelectrolytes

S4 O15
Laurent LERMUSIAUX, Monash University
Self-assembly of gold nanoparticles into structurally different tetramers using a single tetrahedral DNA template

S4 O16
Aimeric OUVRARD, CNRS - University Paris Saclay
Geometrical and Plasmonic Properties of Long-Range Ordered Pd/Au Core/Shell Nanoparticles

S4 O17
Anthony DÉSERT, Laboratoire de Chimie ENS Lyon - Université Lyon 1 - CNRS, UMR 5182
From well-defined plasmonic nanoparticles to hybrid materials for photonic and catalytic applications

S4 O18
Yvonne SOLDO-OLIVIER, CNRS
Plasmonic properties of supported Au and Au-Pd nanoparticles: optical and structural in situ characterization during their growth

S4 O19
Alberto ALVAREZ FERNANDEZ, Centre de Recherche Paul Pascal / Laboratoire de Chimie des Polymères Organiques
Block copolymer based nanoplasmonic surfaces

S4 O20
Ari MAYEVSKY, Monash University
Geometry Dependent Plasmon Resonance Mode Evolution in Crystalline, Faceted Gold Nanotriangle Dimers

S4 O21
Issam KHERBOUCHE, Paris Descartes University
New Advances in Chemistry of Hybrid Plasmonic Nanoparticles

S4 O22
Laura HIPPOLYTE, LCMCP - Sorbonne Université
New synthesis of gold nanoparticles using N-heterocyclic carbene boranes

S4 O23
Leïla BOUBEKEUR-LECAQUE, Laboratoire ITODYS UMR 7086, Université Paris Diderot
Tailoring the shape of core-shell Au-Ag nanoparticles for SERS

S4 O24
Emanuele Alberto SLEJKO, University of Trieste
Thermodynamic Equilibrium and Maximum Yield in Colloidal Nanocrystals Synthesis

S4 O25
Veronique MANY, ICMCB (Institut de Chimie de la Matière Condensée de Bordeaux)
Colloidal Alchemy: Conversion of Polystyrene Nanoclusters into Gold

S4 O26
Umberto MARTINO, Université Paris Diderot, Paris 7, Laboratoire ITDODYS
Assembly of Janus Gold-Silica plasmonic particles

S4 O27
Maroua BEN HADDADA, Université Paris 13
Novel synthesis and characterization of doxycycline-loaded gold nanoparticles. The golden doxycycline for antibacterial applications

S4 O28
Xavier FENOUILLET, CEMES-CNRS
The Gold Ampicilin Interface At the Nanoscale : A Numerical Simulation Study

S4 O29
Karolina MAJSTERKIEWICZ, Malopolska Centre of Biotechnology, Jagiellonian University
Understanding the role of gold in production of ordered protein assemblies

S4 O30
David MARTROU, CNRS / CEMES / GNS

Stabilization of Au Monatomic-High Islands on the (2×2)-Nad Reconstructed Surface of Wurtzite AlN(0001)

S4 O31
Neus G. BASTÚS, Institut Català de Nanociència i Nanotecnologia
Size-Controlled Synthesis of Citrate-Stabilized Gold Nanoparticles: Surface Reactivity, Optical and Catalytic Properties.

S4 O32
Luis LIZ-MARZÁN, CIC BiomaGUNE
Gold Nanorods with Ultranarrow LSPR Bands

S4 O33
Fabienne TESTARD, CEA
Twinned Gold Nanoparticles under Growth: Bipyramids Shape Controlled by Environment

S4 O34
Denis CHATEAU, ENS Lyon
Gold nanobipyramids and beyond : highly concentrated, near quantitative synthesis of pentatwinned nanostructures.

S4 O35
Santosh Kumar MEENA, Université de Lyon, CNRS, École Normale Supérieure de Lyon, UMR 5182
Implications on the growth of gold bipyramid nanoparticles from molecular dynamics simulations

S4 O36
Mona TREGUER-DELAPIERRE, ICMCB-CNRS, University of Bordeaux
How to synthesize gold nanocages with a precise number of windows ?

S4 O37
Clément DULONG, MONARIS, UMR 8233, Sorbonne Université Sciences
From Au or Ag clusters to nanoparticles: an ab initio and atomistic study

S4 O38
Katsuaki KONISHI, Hokkaido University
Au···H hydrogen bonds in ligand-coordinated gold clusters

S4 O39
Chao LIU, Dalian Institute of Chemical Physics, CAS
One-pot Synthesis and Structure of Au23-xAgx(SR)15 Nanocluster

S4 O40
Ian HAMILTON, Wilfrid Laurier University
A series of intrinsically chiral gold nanocage structures

S4 O41
Nadezhda NIKITINA, Moscow State University
The active centers of oxygen adsorption on thiolate-protected gold clusters in various solvents

Self-assembly of gold nanorods in ordered spherical supraparticles

J.E.S. van der Hoeven[1,2], Y. Liu[1], M. Bransen[1], D.A.M. de Winter[1], M.A. van Huis[1], P.E. de Jongh[2], A. van Blaaderen[1]

(1) *Soft Condensed Matter, Utrecht University, Utrecht, Netherlands*

(2) *Inorganic Chemistry and Catalysis, Utrecht University, Utrecht, Netherlands*

Gold nanoparticles exhibit interesting optical properties which arise from their localized surface plasmon resonance. In particular anisotropic Au nanoparticles, such as Au nanorods (NRs), have enhanced and highly tunable plasmonic properties due their longitudinal surface plasmon resonance in the visible and near-infrared range of the spectrum. This makes Au nanorods suitable materials for numerous optical applications such as surface-enhanced Raman spectroscopy (SERS) [1], data storage [2], photo catalysis and medical photo thermal applications. Recently, it has been shown that performance of AuNRs in Raman spectroscopy can significantly be enhanced when placing the NRs in close proximity in large colloidal crystals, whereby plasmonic hotspots of the individual NRs overlap and strongly enhanced plasmonic hotspots are created [3].

Here, we present the synthesis of spherical colloidal crystals, so-called supraparticles, of variable size consisting of silica coated AuNRs (Figure 1). The aim of the study is to compare supraparticles with and without overlapping plasmonic hotspots between the AuNRs in their performance in Raman spectroscopy. To this end, silica coated AuNRs with either a 15-20 nm thick mesoporous silica shell or a 3-4 nm thin silica shell were assembled in supraparticles. The self-assembly was done by using a solvent evaporation method [4], whereby a polar dispersion of rods was emulsified in a larger apolar phase. By slowly evaporating the polar phase, the AuNRs in the shrinking droplets assembled into spherical supraparticles. The 3D-structure of these assemblies was studied in detail with advanced electron microscopy techniques such as HAADF-STEM tomography and FIB-SEM slice and view, allowing us to track the position and orientation of the NRs [5]. First, we show the aspect ratio of the rods strongly influences the degree of order in the orientation of the rods, where the orientation of the rods changes from random- to smectic order when increasing the aspect ratio of the rods. Second, we compared the enhancement of crystal violet in Raman spectroscopy in the presence of supraparticles with and without overlapping hotspots and detect much higher Raman signals in the structures composed of thin silica coated AuNRs compared to the supraparticles of thick silica coated AuNRs.

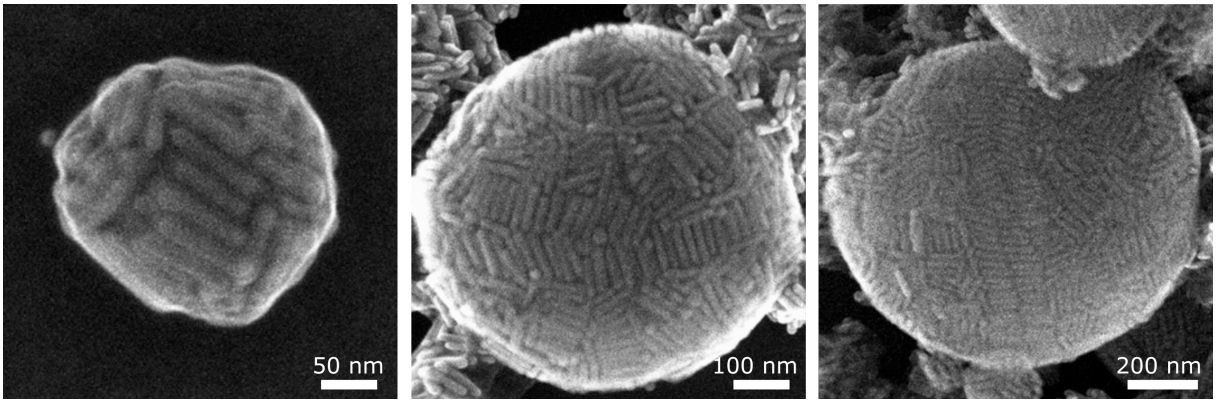


Figure 1. Electron microscopy images of ordered spherical supraparticles synthesized via the self-assembly of 3-4 nm thin silica coated Au nanorods

References

1- M.N. Sanz-Ortiz, ACS Nano, 9 (2015), 10489–10497
2- P. Zijlstra et al., Nature, 459, (2009), 410–413
3- C. Hamon et al., Nanoscale, 8, 2016, 7914
4- B. de Nijs/S. Dussi, A. Van Blaaderen et al., Nature Materials, 14, (2015), 56–60
5- T. Besseling, A. Van Blaaderen et al., J. Phys. Condens. Matter, 27 (2015), 194109

Corresponding author email: j.e.s.vanderhoeven@uu.nl

Chiral gold nanoparticle superstructures directed by silica nanohelices: towards innovative chiroptical properties

J. Gao[1], E. Pouget[1*], R. Oda[1]
(1) *Institute of Chemistry & Biology of Membranes & Nanoobjects (UMR5248 CBMN), CNRS / Bordeaux University, Pessac, France*

In nano-photonics, gold nanoparticle assemblies exhibit strong resonances in the visible range. If these assemblies are chiral, the strong coupling of localized plasmon resonance between nanoparticles along the imposed geometrical arrangement locally enhances the chiroptical coupling to light by orders of magnitude compared to naturally-occurring materials, yielding interesting values of circular dichroism and optical activity. Most of these existing chiral gold nanoparticle nano-structures are based on organic scaffolds as DNA or peptides,[1] which generally suffer from vulnerability (chemically, mechanically and thermally), calling for more robust and 3D anisotropic scaffolds as better candidates for the organization of nanoparticles to fabricate nanophotonic materials. In the present work, we propose an alternative route to fabricate new chiral plasmonic nano-objects based on silica nano-helices with finely tunable morphologies covered with calibrated gold nanoparticles (see figure 1).[2] These chiral plasmonic nano-objects are studied first as individual objects then as 2D and 3D hierarchically organized structures. Their plasmonic and chiroptical responses are assessed by optical measurements.

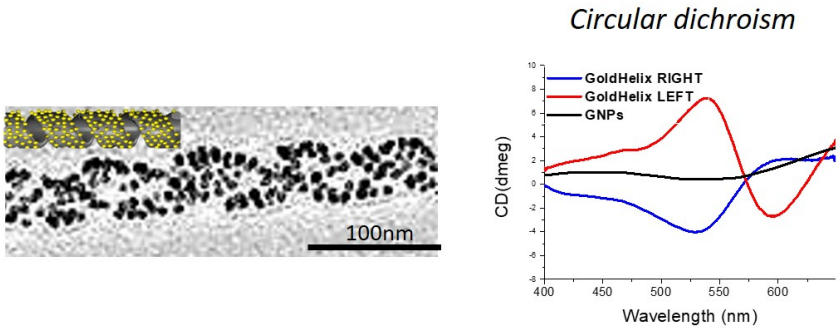


Figure 1. Gold nanoparticles helicoidally organized on silica nanohelix template and the corresponding chiroptical spectra.

References

1- (a) Zhang S. et al., *Adv. Func. Mater.*, 17, 3258 (2007), (b) Song C. et al., *NanoLett.*,13, 3256 (2013), (c) Qi H. et al., *J. Am. Chem. Soc.*, 133, 3728 (2011), (d) Kuzyk A. et al., *Nature*, 483, 7389, (2012), 311, (e) Schreiber R. et al., *Nature Comm*, 4, 2948 (2013)

2- Cheng J. et al., *ACS Nano*, 11(4), 3806-3818 (2017)

Corresponding author email: e.pouget@cbmn.u-bordeaux.fr

Ultrathin gold nanowires: growth mechanism and self-assembly

R. Ramamoorthy,[1] Said Nouh,[1] J. Vargas Tellez,[2] P. Roblin,[3] L.-M. Lacroix,[1] S. Teychene,[3] M. Imperor,[4] R. Poteau,[1] V. Petkov,[2] G. Viau[1*]

(1) *Université de Toulouse, LPCNO, UMR 5215 INSA CNRS UPS, Toulouse, France*
(2) *Department of Physics, Central Michigan University, Mt. Pleasant, Michigan, United States*
(3) *Université de Toulouse, LGC, CNRS, INPT, UPS, Toulouse, France*
(4) *Laboratoire de Physique de Solides, UMR 8502, Université Paris-Sud, Orsay, France*

Ultrathin gold nanowires (NWs), exhibiting a diameter of 1.7 nm and a micrometric length, have attracted expanding interests due to their unique properties, as high surface-to-volume ratio, mechanical flexibility and remarkable conductivity properties, with applications for electrical sensors or transparent electrodes [1,2]. Their very small diameter, very high aspect ratio (>1000) and the great importance of the ligand shell organization both on their growth and stability make these fascinating objects intermediates between metal and 1D supramolecular organization (Fig. 1).
The synthesis is a simple reduction of $HAuCl_4$ in a solution of oleylamine in hexane at room temperature facilitating *in situ* measurements [3]. NW growth and self-assembly into hexagonal arrays were followed by *in situ* small angle X-ray scattering (Fig. 2). The growth rate was found to strongly depend on the solvent. The lattice parameter of the hexagonal phase and the interwire distance varied in the range 9-10 nm and 7.3-8.3 nm, respectively, showing that a bi-layer of oleylamine coats the wires during the growth [4]. We showed also that the interwire distance could be monitored in the range 2.5-8.3 nm thanks to ligand exchange at the wire surface [5]. The atomic structure of the gold core of the ultrathin NWs is still under debate. A fcc structure with stacking faults was reported by HRTEM studies but the Au NWs faced a strong instability and a recrystallization process under the electron beam was observed [6]. Recent *in situ* WAXS measurements and PDF analysis revealed a non-compact structure. Several structural models are under investigation to fit the PDF patterns that could shed new light on the growth mechanism and the electronic properties.

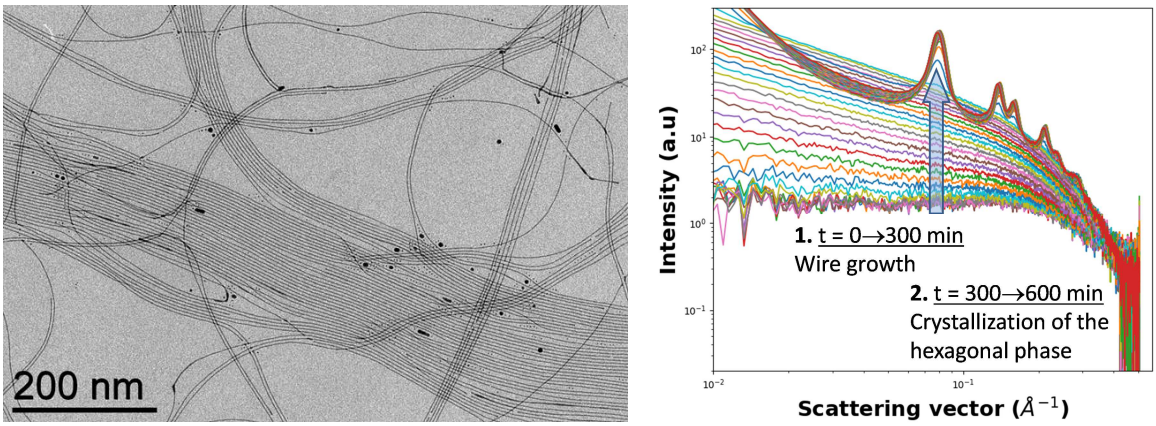


Figure 1. (a) TEM image of ultrathin gold nanowires (b) SAXS pattern measured during the ultrathin gold nanowires synthesis at room temperature in toluene.

References

1- A. Loubat, W. Escoffier, L.-M. Lacroix, G. Viau, R. Tan, J. Carrey, B. Warot-Fonrose, B. Raquet, Nano Research **6**, 644 (2013).
2- P. Moutet, L.-M. Lacroix, A. Robert, M. Impéror-Clerc, G. Viau, L. Ressier, Langmuir **31,** 4106 (2015).
3- A. Loubat, L.-M. Lacroix, A. Robert, M. Impéror-Clerc, R. Poteau, L. Maron, R. Arenal, B. Pansu, G. Viau, J. Phys. Chem. C **119**, 4422 (2015).
4- A. Loubat, M. Impéror-Clerc, B. Pansu, F. Meneau, B. Raquet, G. Viau, L.-M. Lacroix, Langmuir **30**, 4005 (2014).
5- El S. Nouh, E. Baquero, L. –M. Lacroix, F. Delpech, R. Poteau, G. Viau, Langmuir **33**, 5456 (2017).
6- L.-M. Lacroix, R. Arenal, G. Viau, J. Am. Chem. Soc. **136**, 13075 (2014).

Corresponding author email: gviau@insa-toulouse.fr

Self-Assembly of Polymer-Coated Gold Nanoparticles

F. Schulz[1,2*], M. A. Schroer[3], F. Lehmkühler[2,4], J. Möller[5], G. Grübel[2,4], H. Lange[1,2]
(1) *Institute for Physical Chemistry, University of Hamburg, Grindelallee 117, 20146 Hamburg, Germany.*
(2) *The Hamburg Centre for Ultrafast Imaging (CUI), Luruper Chaussee 149, 22761 Hamburg, Germany.*
(3) *European Molecular Biology Laboratory (EMBL) Hamburg c/o DESY,Notkestr. 85, 22607 Hamburg, Germany.*
(4) *Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany.*
(5) *European X-Ray Free-Electron Laser Facility, Holzkoppel 4, 22869 Schenefeld, Germany.*

Self-Assembly of nanoparticles (NP) is a promising tool for the synthesis of new materials with tailored properties.(*1*) Using polymer-ligands provides additional possibilities to direct the self-assembly and tune the mechanical, electrical or optical/plasmonic properties of the resulting materials. In the case of gold nanoparticles (AuNP), the plasmonic properties are especially interesting for surface-enhanced spectroscopies and fundamental studies. Two recent studies will be presented. In the first study we show that it is possible to obtain well-ordered, mono- and multilayer films of AuNP coated with polystyrene-based ligands (PS), with AuNP diameters up to 45 nm. Monolayers > $2x10^4$ μm^2, and freestanding films > $1.6x10^3$ μm^2 were obtained. The role of ligand size for functionalization and self-assembly of AuNP ranging from 6-90 nm in diameter was tested.(*2*) In the second study based on recent works (*3, 4*) we observed the crystallization of poly(ethylene glycol) (PEG) coated AuNP in solution induced by hydrostatic pressure. This new effect was studied by small-angle X-ray scattering (SAXS) and we describe a parameter study resulting in a phase diagram for the system.

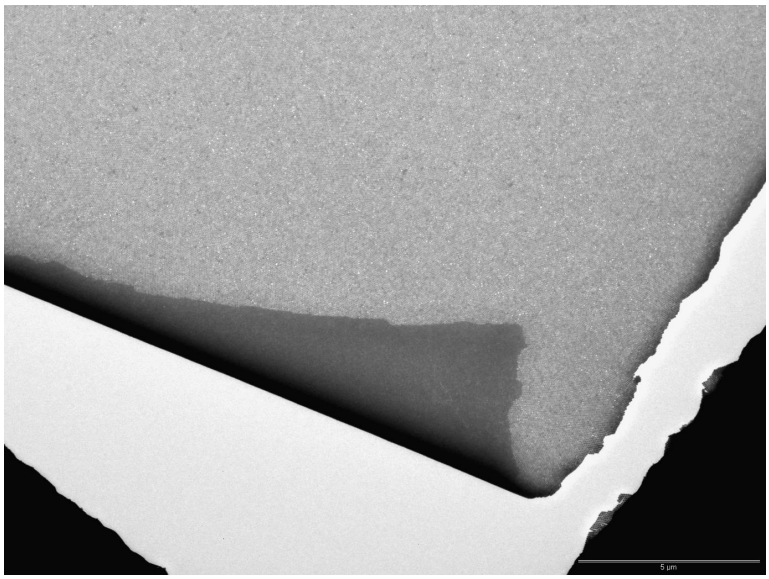


Figure 1. Freestanding monolayer film of polystyrene-coated AuNP (d ~ 45 nm)

References

1 M. A. Boles, M. Engel, D. V. Talapin, *Chem. Rev.* **116**, 11220–11289 (2016).
2 F. Schulz, S. Tober, H. Lange, *Langmuir*. **33**, 14437–14444 (2017).
3 F. Schulz *et al., Part. Part. Syst. Charact.* **35**, 1700319 (2017).
4 M. A. Schroer *et al., J. Phys. Chem. C*. **120**, 19856–19861 (2016).

Corresponding author email: Florian.Schulz@chemie.uni-hamburg.de

Colloidal Design of Hierarchical Plasmonic Nanostructures

C. Hamon[1*], C. Goldmann[1], Doru Constantin[1]
(1) *Laboratoire de Physique des Solides, Univ. Paris-Sud, CNRS, UMR8502, 91405, Orsay, France*

The growing interest on plasmonic nanoparticles (Au, Ag) revolve around their optical features that are dramatically affected when the conduction electrons collectively oscillate in resonance with the frequency of incident light. This phenomenon is known as localized surface plasmon resonance which leads to intense colors in the far field and strong electromagnetic fields at the surface of the particles. Moreover, enhanced plasmonic properties can be obtained when nanostructures are located at very short distances, increasing dramatically the electromagnetic fields at interparticles gaps. Among the diversity of possible plasmonic architectures, gold nanorods supercrystals are particularly interesting for plasmon enhanced spectroscopy.[1, 2] In this presentation, recent work will be presented in which we aim at tuning the assembly of plasmonic nanostructures to ultimately generate new collective optical properties. In particular, core@shell Au@Ag anisotropic particles have been prepared by wet chemistry approaches. Starting from colloidal suspensions, solid or colloidal material are obtained with a controlled hierarchical organization (Figure 1). The supercrystals lattice parameter and local organization is tuned depending on the thickness of the Ag layer and investigated by complementary techniques (SAXS, TEM). We believe those nanostructures to be of interest for the broad range of applications beneficiating from plasmonic materials.

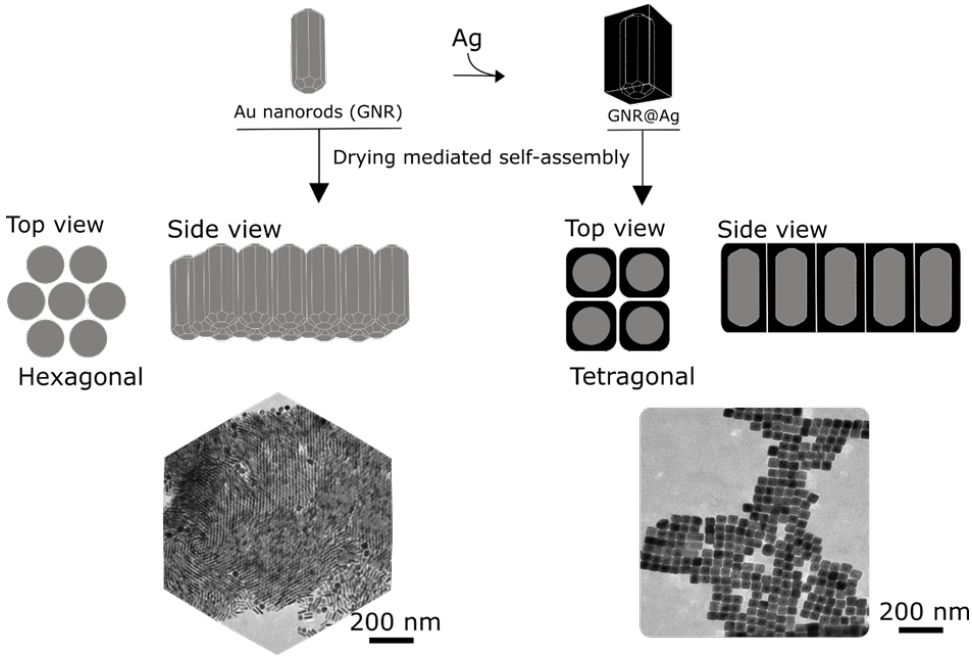


Figure 1. Concept of the proposed work. Gold nanorods are prepared by colloidal chemistry and coated with an Ag shell. This transform the morphology of the nanoparticles which evolves from an octagonal cross section to a square cross section. This have important implication when the nanoparticles are assembled on a TEM grid: a hexagonal superlattice is observed for Au nanorods while a tetragonal superlattice is observed in the case of Au@Ag nanorods.

References

1- Hamon, C.; Novikov, S.; Scarabelli, L.; Basabe-Desmonts, L.; Liz-Marzán, L. M. ACS Nano, 8, 10694 (2014)
2- Scarabelli, L.; Hamon, C.; Liz-Marzán, L. M. Chem. Mater. **29**, 15 (2017)

Corresponding author email: hamon@lps.u-psud.fr

Ultrathin Gold Films with High Flexibility Prepared by Irradiation with UV Light on Au NPs Monolayer

T. Kawai*, T. Nishimura, M. Nakagawa
Tokyo University of Science, Tokyo, Japan

Indium tin oxide (ITO) as transparent conductive materials has been used in a wide range of applications, however it cannot be used in optoelectronic devices for ultraviolet (UV) or infrared (IR) light because of a lack of transparency in UV and IR regions. Moreover, ITO electrodes, in general, limit their applications in flexible devices due to their inherent brittleness. One of the most successful bottom-up approaches to these problems is the use of metal nano-materials, particularly one- or two-dimensional metal nanowires, due to their high flexibility and transparency of UV, visible and IR light. However, there have been a few reports on the synthesis methods of metal nanowires 1), and the fabrication of conductive films comprised of nanowires is inefficient because large quantities of the nanowires are required to ensure their conductivity. In this study, we show that free-standing conductive Au films with high transparent can be prepared by irradiating with UV light onto Langmuir monolayers of Au nanoparticles (NPs). We also demonstrate that the resulting free-standing Au films can be put on desired substrates and the sheet resistance of the Au films transferred on filter papers has retained almost constant after 100 cycles of the bending test.

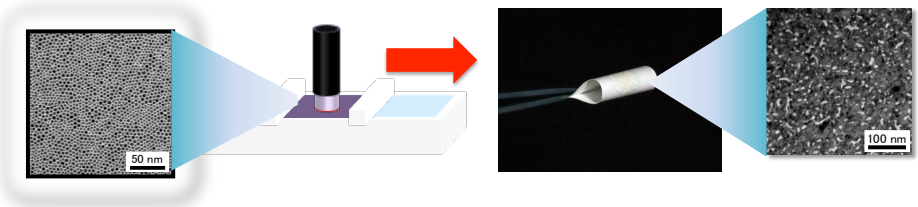


Fig.1 Schematic illustration of the preparation method of ultrathin Au films.

Au NPs monolayer were prepared by spreading a chloroform dispersion of dodecanethiol protected Au NPs with ca.4.5 nm diameter. The resulting Au NPs monolayer was blue, and UV light was irradiated on it by using an optical fiber (Fig.1). We examined the effect of UV light irradiation on the morphology of the NPs monolayer on water. The irradiation with UV light resulted in a considerable morphological change of Au NPs; Au NPs were fused each other in a few minutes, and a gradual progress of the fusion process consequently brought about a complete disappearance of Au NPs and the formation of ultrathin Au films with many tiny holes within 5 min, together with a color change from blue to pale yellow. Here, FT-IR and XPS measurements revealed that UV light caused an oxidative decomposition of dodecanethiol as the protected molecule of Au NPs. Continuous further irradiation with UV light induced a growth of the tiny holes and the formation of nanomesh with dozen nanometers of holes, accompanied by the color change from pale yellow to pale purple. After 20 min there was no significant change in the morphology and color. When UV light was irradiated onto Au NPs monolayer on glass substrates, instead of water, as the control experiment, we obtained no ultrathin films but larger NPs.

The ultrathin Au films had a thickness of 3.5 nm (Fig. 2), and had a high transmittance of ~80 % in the spectral range of 250-900 nm. The films were transferred onto filter papers by Langmuir-Schaefer technique, and the electrical conductivity was measured by four-terminal method. The conductivity was $5*10^3$ S/cm and kept almost constant values after 100 cycles of the bending test, where the repeated bending radius was 0.6 mm.

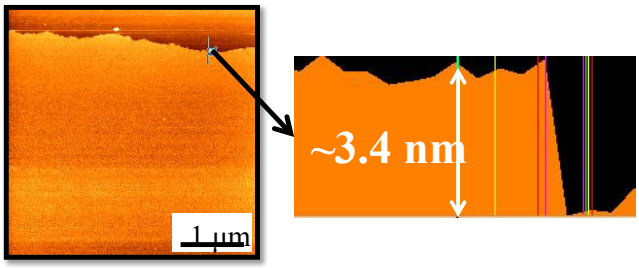


Fig.2 AFM images of ultrathin Au Film

References

1. Y.Imura, T. Kawai, et al., Chem. Commun, **46**, 9206 (2010); Chem. Commun, **47**, 6380 (2011); Langmuir, **28**, 14998 (2012); Langmuir, **29**, 1669 (2013); Langmuir, **30**, 1888 (2014); Langmuir, **30**, 5026 (2014); New J. Chem. **40**, 7048 (2016).

Corresponding author email: kawai@ci.kagu.tus.ac.jp

Ionic Liquid-Sputtering Method to Prepare Au Nanoparticles with Some Configurations

S. Kuwabata[1*], T. Tsuda[1], T. Uematsu[1], T. Kameyama[2], T. Torimoto[2]
(1) *Department of Applied Chemistry, Osaka University, Suita, Osaka, Japan*
(2) *Department of Crystalline Materials Science*, *Nagoya, Japan*

Ionic liquid (IL) is salt staying in liquid phase even at room temperature. Its extremely low vapor pressure allows us to put the liquid in vacuum chambers of analytical and manufacturing instruments. Based on this fascinating feature, we are developing new vacuum technologies with IL. One of them is metal sputtering onto IL to prepare nanoparticles of metal, alloy, and metal oxides, as schematically shown as Figure 1(a). The first attempt was gold sputtering onto typical imidazolium ionic liquid. Color of IL was changed to yellow or red-brown (see Figure 1(b)) after Au-sputtering.[1)] TEM observation of the resulting IL revealed that gold nanoparticles with relatively small size distribution were stably suspended in IL. Simultaneous sputtering of two different metals onto IL gives alloy nanoparticles.[2)] If you would like to take the prepared nanoparticles outside of IL, one way is putting the Au nanoparticles-suspended IL on a carbon substrate with heating, resulting in strong adsorption of nanoparticles on the surface of the carbon materials including plate substrates and powder materials. If the carbon electrodes, on which gold or gold alloy nanoparticles were utilized as electrocatalyst. It was found that the preparation conditions, such as temperature, sputtering rate, and kind of IL influenced the properties of the nanoparticles.[3)]

Recently, we succeeded in preparation of membranous gold nanoparticles by the same sputtering method. This was possible by just using IL having hydroxyl group. For example, sputtering of Au on 1-(2-hydroxyelthyl)-3-methylimidazolium tetrafluoroborate (HyEMI-BF_4) produced an Au particle film on the surface of the IL as shown in Figure 2(a).[4,5)] Some cracks in the film were made by slightly shaking the IL. The obtained Au film could be transferred onto a glass substrate by horizontal liftoff method as shown in Figure 2(b). The IL underneath the film was colorless, indicating that all sputtered Au deposited on the surface of IL. TEM observation of the transferred Au nanoparticles film revealed that the film on the IL was composed of Au nanoparticles and the amount of Au deposited could be controlled by the sputtering time.

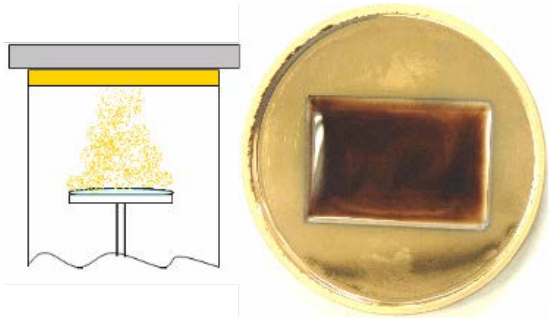


Figure 1 Schematic illustration of gold sputtering onto IL (left (a)) and a picture of IL after Au sputtering (right (b)).

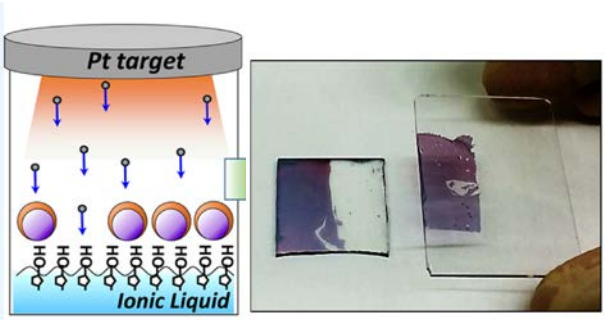


Figure 2 Schematic illustration of gold sputtering onto IL having OH group (left (a)) and a picture of IL after Au sputtering (right (b)).

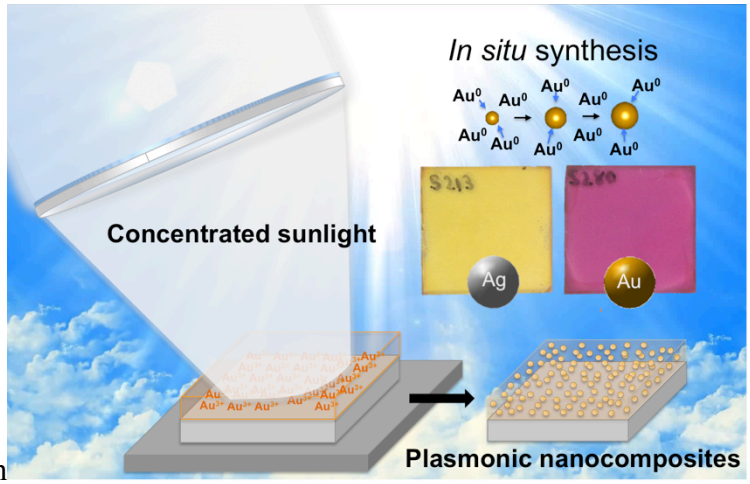
References
1) T. Torimoto, K. Okazaki, T. Kiyama, K. Hirahara, N. Tanaka and S. Kuwabata, *Appl. Phys. Lett.*, 2006, *89*, 3.
2) T. Torimoto, T. Tsuda, K. Okazaki and S. Kuwabata, *Adv. Mater.*, 2010, *22*, 1196-1221
3) K. I. Okazaki, T. Kiyama, K. Hirahara, N. Tanaka, S. Kuwabata and T. Torimoto, *Chem. Commun.*, 2008, 691-693.
4) D. Sugioka, T. Kameyama, S. Kuwabata, and T. Torimoto, *Phys. Chem. Chem.*, 2015, *17*, 13150-13159.
5) D. Sugioka, T. Kameyama, S. Kuwabata, T. Yamamoto, and T. Torimoto, *ACS Appl. Mater. Inter.*, 2016, *8*, 10874-10883.

Corresponding author email: kuwabata@chem.eng.osaka-u.ac.jp

In situ synthesis of plasmonic nanoparticles in polymer thin films under laser and solar irradiation

E. Nadal[1,2,3], L. Peres[1], N. Barros[2,3], K. Soulantica[1], M. Respaud[1], H. Kachkachi[2,3]
(1) *LPCNO (Laboratoire de Physique et Chimie des Nano-Objets), Université de Toulouse, INSA, UPS, CNRS,Toulouse, France*
(2) *PROMES (PROcédés Matériaux et Energie Solaire), CNRS UPR 8521, Perpignan, France*
(3) *Université de Perpignan Via Domitia, Perpignan, France*

Plasmonic nanocomposite materials are of great interest in many applications such as photonics, photovoltaics, catalysis, medicine and biology. This field has been the subject of a large activity in the past decades. At the same time, chemists have demonstrated the versatility of wet synthesis approaches to fabricate nanoparticles with well-defined magnetic and optical properties. However, the insertion in matrices of such nanostructures on a large scale and at high concentrations in view of applications is still challenging.
In order to address this issue, we developed two original fabrication techniques based on *in situ* synthesis of nanoparticles in polymer films under irradiation. In these approaches, the nanoparticle are synthesized by introducing metallic precursors directly in the polymer matrix before film deposition by spin coating. The precursors are then photo-reduced under irradiation and a simultaneous or subsequent annealing triggers the nanoparticle growth. In the first approach, our aim is to control the spatial organization of the nanoparticles within the polymer films by laser interferometry. We show that the gold nanoparticle gratings thus formed present unusual diffractive properties that strongly depend on the plasmonic excitation of the system[1]. In the second method, we study the *in situ* synthesis of plasmonic nanoparticles in polymer thin films under concentrated solar irradiation. We show that this technique can be used as an efficient route for the fabrication of gold and silver nanoparticles in several types of polymer matrix[2]. Moreover, we found that adjusting irradiation conditions, and especially the light flux, affects the size and morphology of the nanoparticles and therefore influences the optical properties of the system. Regarding the applications, this approach can be readily used for large-scale production and allows for the insertion of large metal filling fractions in the polymer films while keeping the nanoparticles from agglomeration. Finally, we have successfully tested this approach by using biopolymer as matrices, thus meeting the requirements of green synthesis.



m

Figure 1. Principle of the in situ synthesis of gold nanoparticles under concentrated solar irradiation

References

1 E. Nadal, N. Barros, H. Glénat, J. Laverdant, D. S. Schmool and H. Kachkachi, *J. Mater. Chem. C*, , **5**, 3553–3560 (2017).

2 E. Nadal, L. Peres, N. Barros, V. Goetz, K. Soulantica, M. Respaud and H. Kachkachi. "In situ synthesis of plasmonic nanocomposites under cocentrated solar irradiation" (In peer review).

Corresponding author email: elie.nadal@insa-toulouse.fr

Double-Target Sputtering for Au Containing Alloy Nanoparticles

M. T. Nguyen and T. Yonezawa
Division of Materials Science and Engineering, Faculty of Engineering, Hokkaido University, Kita 13 Nishi 8 Kita-ku, Sapporo, 060-8628, Japan

Au and its alloy nanoparticles received great interest in catalyst, plasmonics, biotechnology, and etc. In our research we have studied a new green method to produce metal alloy nanoparticle dispersion, in particular Au alloys, called double target sputtering onto liquid polymers. This is based on vacuum sputtering technique to generate atoms/clusters from the two metal targets followed by the collision of different elemental metal atoms/clusters in gas phase and liquid/gas interface to form bimetallic alloy nanoparticles. Our double-target set-up allows simultaneous sputtering of Au and other metal, such as Ag, Cu, to form Au alloy nanoparticles. In addition, the design offers separately control of sputter current to each metal target as a tool to control the composition of the alloy nanoparticles. In general, a less or non-volatile liquid inserted in vacuum chamber is needed to collect the alloy nanoparticles and at the same time hinder the particle growth by high viscosity and protecting function of the liquid. Here, liquid polyethylene glycol, PEG, M. W. = 600 was chosen as the liquid substrate for stabilizing the sputtered alloy nanoparticles. We obtained tailorable composition of Au/Ag and Au/Cu alloy nanoparticles dispersed in PEG via applying different sputter currents for each metal target. We found that positions of localized surface plasmon resonance peak of PEG containing Au/Ag nanoparticles were linearly varied with the compositions of the sputtered nanoparticles, which is an indication of Au/Ag alloy formation. In addition, we confirmed the Au/Ag alloy in individual nanoparticles with the STEM-EDS mappings with uniform distribution of two metals for entire nanoparticles being observed (Figure 1). Similar results were demonstrated for Au/Cu nanoparticles via double target sputtering (Figure 1). Difference from Au and Ag which make complete solid solutions, Au and Cu form intermetallic compounds in the bulk state. Thus, the formation of Au/Cu random alloy nanoparticles with tailorable composition at room temperature via sputtering is very interesting. This demonstrated that our double target sputtering onto PEG can be a potential approach in bimetal alloy nanoparticle synthesis.[1,2]

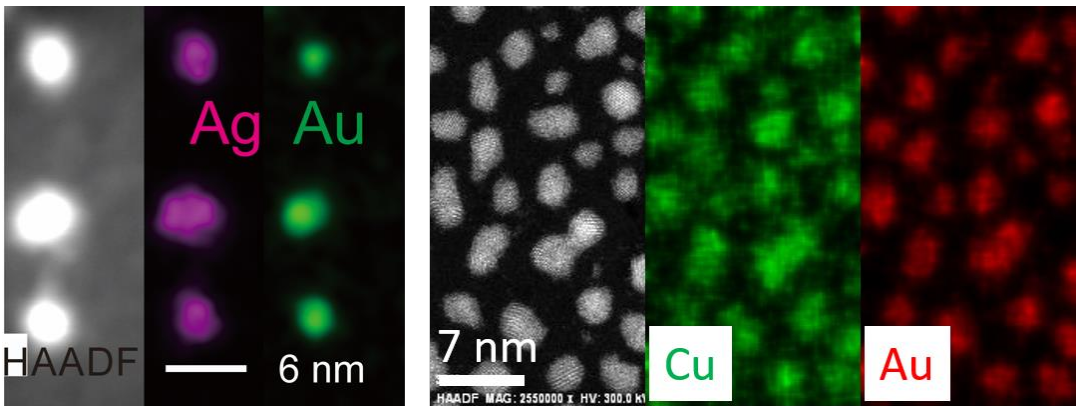


Figure 1. HAADF and STEM-EDS elemental mapping images of Au/Ag and Au/Cu alloy nanoparticles prepared via sputtering

References
1- M. T. Nguyen, T. Yonezawa, Y. Wang, T. Tokunaga, Mater. Lett. **171**, 75 (2016).
2- M. T. Nguyen, H. Zhang, L. Deng, T. Yonezawa, T. Tokunaga, *Langmuir* **33**, 12389 (2017).

Corresponding author email: mai_nt@eng.hokudai.ac.jp

Surface Chemistry Of Colloidal Surfactant-Free Gold Nanoparticles Generated By Laser Ablation

M. Patanen[1], J. Gaudin[2], I. Papagiannouli[2], V. Blanchet[2], R. Grisenti[3], G. Laurens[4], D. Amans[4], C. Nicolas[5], A. R. Milosavljević[5], E. Robert[5], J. D. Bozek[5], M. De Anda Villa[6], S. Macé[6], S. Steydli[6], C. Prigent[6], E. Lamour[6], D. Vernhet[6], M. Trassinelli[6], A. Lévy[6]

(1) *Nano and molecular systems research unit, Faculty of Science, P.O. Box 3000, 90014 University of Oulu, Finland*

(2) *Univ. Bordeaux, CNRS, CEA, CELIA (Centre Lasers Intenses et Applications), UMR5107, 33405 Talence, France*

(3) *Institut für Kernphysik, J. W. Goethe Universität Max-von-Laue-Str. 1, 60438 Frankfurt (M), Germany*

(4) *Institut Lumière matière, UMR5306 - UCBL - CNRS, 10 rue Ada Byron, 69622 Villeurbanne CEDEX, France*

(5) *Synchrotron SOLEIL, l'Orme des Merisiers Saint Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France*

(6) *Sorbonne Université, CNRS UMR 7588, Institut des Nanosciences de Paris (INSP), 75252 Paris Cedex 05, France*

Surfactant free gold nanoparticles (AuNPs) have been synthetized by Pulsed Laser Ablation in Liquids (PLAL). This versatile technological approach is an alternative to the commonly used chemical reduction synthesis. PLAL provides ligand-free AuNPs which are of great interest for several applications. The surface chemistry occurring on these surfactant-free AuNPs is of primary importance not only to develop the associated technological applications but also to understand the origin of the colloidal stability. We will present here recent results of the surface characterization using a very surface sensitive characterization technique, namely synchrotron radiation excited photoelectron spectroscopy. We have studied the surface composition/oxidation of gold NPs produced in aqueous solutions different salinities and pH. The colloidal suspension prepared using PLAL is aerosolized and a free-standing AuNP beam is studied, avoiding the influence of substrate or solvent. We have found signatures of halide-ions and possible gold oxidized atoms on the surface of the AuNPs. The demonstrated technique provides a promising new way to study bare gold surfaces and a complementary insight to colloidal stability.

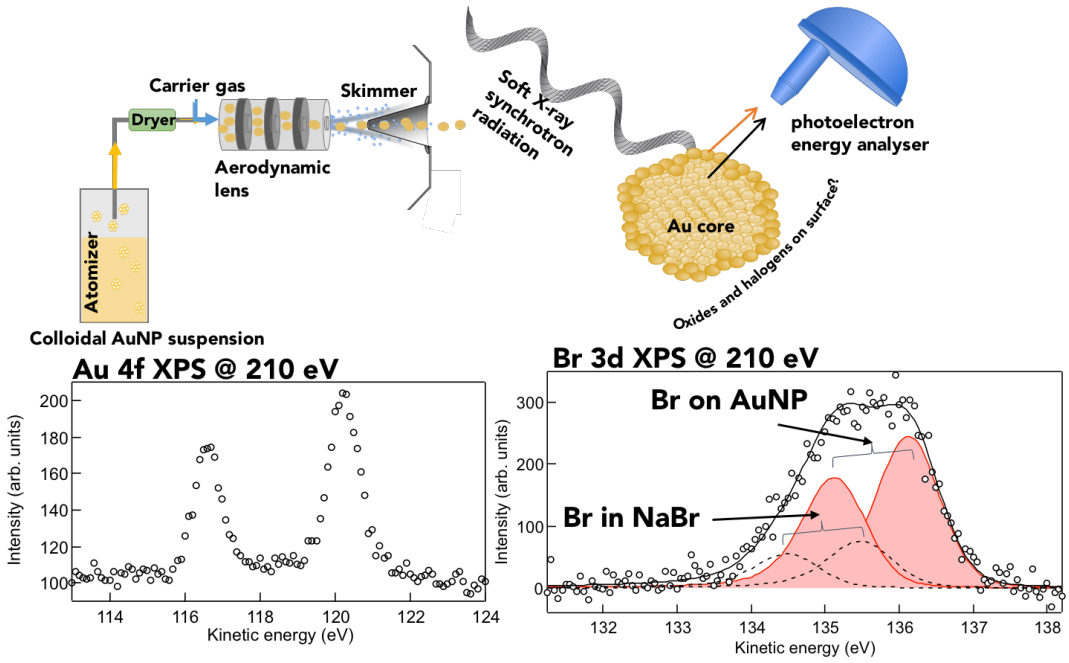


Figure 1. An aerosol of AuNPs is created using an atomizer. An aerodynamic lens focuses the AuNP beam to the interaction region with soft X-rays of PLEIADES beamline (Synchrotron SOLEIL). The Au 4f and Br 3d photolines are recorded with a hemispherical electron analyzer to learn from the bonding between AuNPs and the ionic species believed to be responsible for the colloidal stability.

Corresponding author email: minna.patanen@oulu.fi

Insertion of gold nanoparticles within bulk graphite based on peculiar hydrophobic interactions

L. Ardemani, L. Michel, G. Genay, V. Caps*

ICPEES (Institut de Chimie pour l'Energie, l'Environnement et la Santé), CNRS UMR 7515 / University of Strasbourg, 25 rue Becquerel, 67087 Strasbourg Cedex 02, France

Gold nanoparticles (Au NPs) are usually associated with oxide supports which make them catalytically active for the oxidation of CO at low temperature.[1] The stability of these materials however is poor, due to poisoning of the gold/support interface by *in situ* formed carbonate-type species.[2] Surface hydroxyl functions are thought to play an active role in the formation of such species.[3] On the other hand, hydrophobic gold catalysts have been shown to exhibit a much higher stability with time-on-stream.[4] The future development of gold catalysis is thus expected to rely on the design of such hydrophobic nanocomposites.

We have recently shown that methylated silica, as well as few layer graphenes, could be decorated with Au NPs upon direct sodium borohydride reduction of triphenylphosphine gold chloride ($AuPPh_3Cl$) in the presence of the hydrophobic support.[5] Here we show that bulk natural graphite (NG) may straight-forwardly be both exfoliated and decorated with *in situ* formed Au NPs by adding a gold precursor and $NaBH_4$ to sonochemically-destabilized NG suspensions. We will present an extensive parametric study involving a series of gold precursors ($AuPPh_3Cl$, $NaAuCl_4$, $KAuCl_4$, $AuCl_3$, $AuBr_3$ and $Au(CH_3COO)_3$) and the systematic structural characterization (ICP, FTIR, Raman, XRD, TGA) of the gold, borax and graphitic components of the resulting solid-state nanocomposite. We will show that the incorporation process relies on the affinity of the gold surface with boron-based anions on one side[6] and, for the first time, on a soft non-covalent bond between the sodium cation and the graphene surface on the other side. Finally, we will discuss the implications for the synthesis of gold-based catalysts and electrocatalysts of such soft, cation-π -based decoration of pristine graphenic surfaces, with regard to typical covalent[7] and π-π[8] functionalizations.

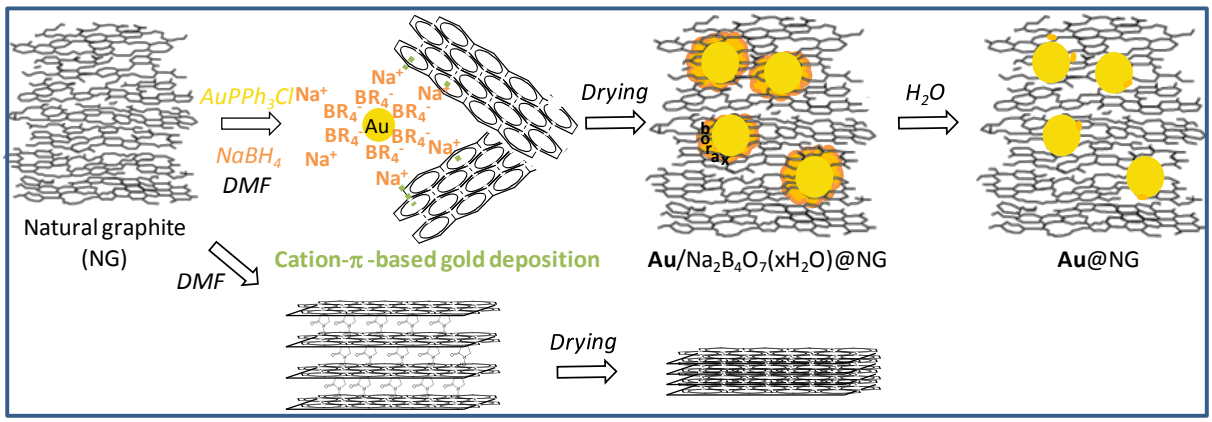


Figure 1. Mechanism of $NaBH_4$-driven insertion of Au NPs within bulk natural graphite.

References

1- M. Haruta, Gold Bull. **37**, 27 (2004).
2- C. W. Corti, R. J. Holliday, D. T. Thompson, Top. Catal. **44**, 331 (2007).
3- C. K. Costello, M. C. Kung, H.-S. Oh, Y. Wang, H. H. Kung, Appl. Catal. A **232**, 159 (2002).
4- P. Laveille, K. Guillois, A. Tuel, C. Petit, J.-M. Basset, V. Caps, Chem. Commun. **52**, 3179 (2016).
5- F. Vigneron, A. Piquet, W. Baaziz, P. Ronot, A. Boos, I. Janowska, C. Pham-Huu, C. Petit, V. Caps, Catal. Today **235**, 90 (2014).
6- C. Deraedt, L. Salmon, S. Gatard, R. Ciganda, R. Hernandez, J. Ruiz, D. Astruc, Chem. Commun. **50**, 14194 (2014).
7- G. Goncalves, P. A. A. P. Marques, C. M. Granadeiro, H. I. S. Nogueira, M. K. Singh, J. Grácio, Chem. Mater. **21**, 4796 (2009).
8- C. Vriamont, T. Haynes, E. McCague-Murphy, F. Pennetreau, O. Riant, S. Hermans, J. Catal. **329**, 389 (2015).

Corresponding author email: caps@unistra.fr

Light-induced response in DNA-nanoparticle crystals

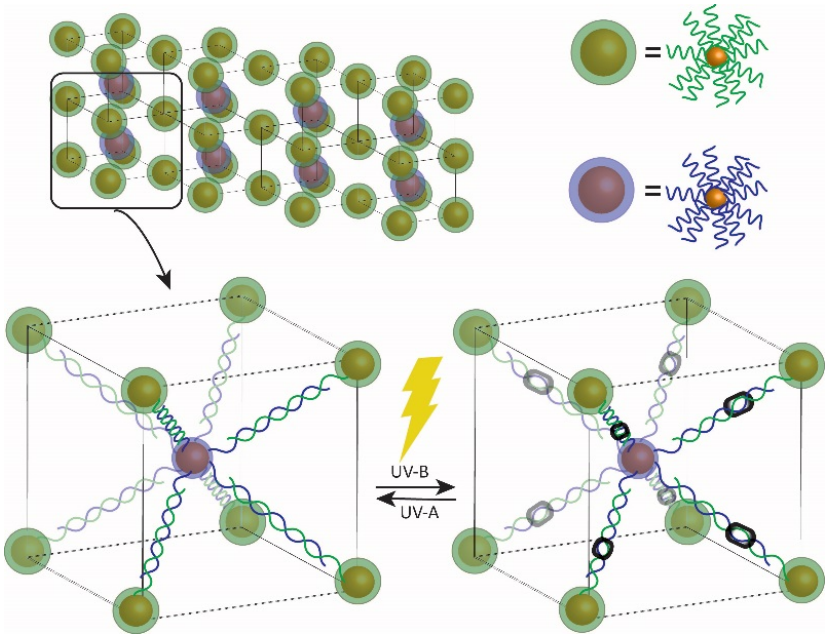
Angela F. De Fazio[a], Afaf H. El-Sagheer[b,c], Jason Kahn[e,f], Tom Brown[b], Otto L. Muskens[a], Oleg Gang[e,f], Antonios G. Kanaras[a]

[a] Physics and Astronomy, Faculty of Physical Sciences and Engineering, University of Southampton, Southampton, SO17 1BJ, UK. [b] Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Oxford, OX1 3TA, UK. [C] Chemistry Branch, Department of Science and Mathematics, Faculty of Petroleum and Mining Engineering, Suez University, Suez 43721, Egypt.

The ability to assemble nanoparticles into programmed 2D or 3D structures by meaning of synthetic oligonucleotides(*1–3*) has resulted into the fabrication of novel nanomaterials with unique physical and chemical properties. In particular this bottom-up approach allows routes to flexible and precise design of featured materials which can be tuned by varying the constituent building blocks. These combine the advanced programming of the assembly processes to the use of innovative ligation techniques.

Despite the promising results achieved towards the engineering of different shaped materials(*4*), by using different size, shape(*5*, *6*) and composition(*7*) particles, DNA-nanoparticles materials lack in stability, which limits their application.

Herein we present a method to fabricate light-responsive self-assembled materials based on synthetic oligonucleotides and metallic nanoparticles endowed with enhanced stability thanks to the introduction of a tunable covalent bond within the sequences. This opens the way to a broad series of possible applications, including their use on surfaces coating and incorporation in hybrid systems.



References

1. A. P. Alivisatos *et al.*, *Nature*. **382**, 609–11 (1996).
2. S. Y. Park *et al.*, *Nature*. **451**, 553–556 (2008).
3. C. A. Mirkin, R. L. Letsinger, R. C. Mucic, J. J. Storhoff, *Nature*. **382**, 607–609 (1996).
4. W. Liu *et al.*, *Science.* **351**, 582–586 (2016).
5. M. N. O'Brien, M. R. Jones, B. Lee, C. a. Mirkin, *Nat. Mater.* **14**, 833–839 (2015).
6. M. R. Jones *et al.*, *Nat. Mater.* **9**, 913–917 (2010).
7. D. Sun, O. Gang, *J. Am. Chem. Soc.* **133**, 5252–5254 (2011).

Corresponding author email: a.f.defazio@soton.ac.uk

DNA-origami mediated self-assembly of nanoelectronic circuits

R. Weichelt[1,3], J. Ye[2,3], Vladimir Lesnyak[1], Nikolai Gaponik[1], Ralf Seidel[2,3], Alexander Eychmüller[1,3]

(1) Physical Chemistry, Technische Universität Dresden, Dresden, Germany
(2) Molecular Biophysics, University of Leipzig, Leipzig, Germany
(3) Center for Advancing Electronics Dresden (cfaed), Dresden, Germany

Driven by Moore´s Law, performance and density of integrated circuits have dramatically increased over the past fifty years. But conventional top-down lithography fabrication methods are losing their appeal due to rising costs, high energy consumption, as well as physical and technical limitations. Alternatives need to be developed, to overcome a cost explosion and to set a new standard for today's smart technology world. One promising way is the introduction of bottom-up techniques for the fabrication of nanoelectronic circuits. In particular, smart building blocks can be self-assembled by the means of DNA-Nanotechnology. A common strategy is DNA origami that serves as a molecularly defined "breadboard", to organize various nanomaterials into hybrid systems.[1] Having a self-assembled, programmable framework allows for the development of nanomaterial constructions with control over dimensions, stoichiometry, orientation, shape and composition. Based on the idea of using DNA-origami molds for the seeded growth of Gold nanoparticles (Au NPs)[2] our work introduces the self-assembly of semiconducting nanomaterials, e.g. Cadmiumsulfide nanorods (CdS NRs) with 40 nm length and 4 nm thickness (see Figure 1). We also show the possibility to assemble two different materials, namely CdS NRs and Au NPs into one DNA-origami mold structure by the means of different oligonucleotide sequences. In addition, we demonstrate the subsequent assembly of our smart building blocks for the build-up of more complex systems, followed by a seeded-growth procedure that allows for electrical contacting using electron beam lithography. We think that our strategy provides an elegant way towards the development of unprecedented nanoelectronic structures.

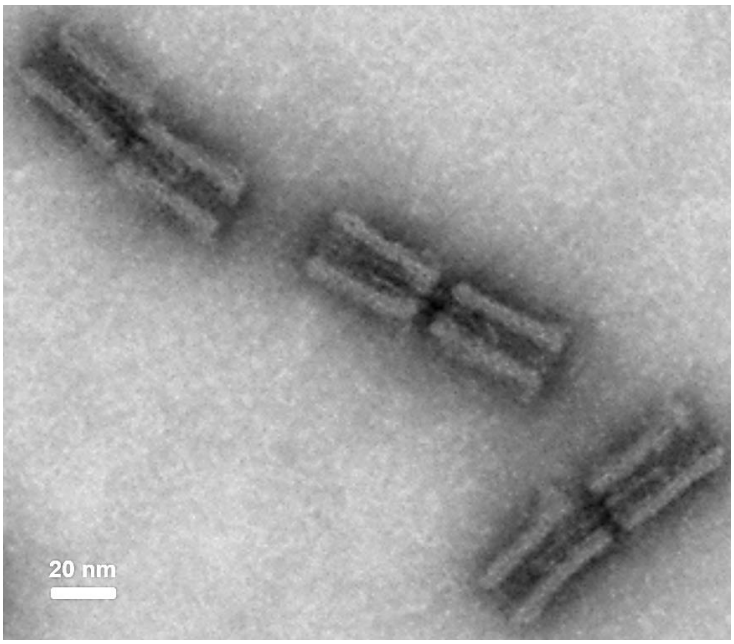


Figure 1. TEM images of self-assembled smart building blocks, containing CdS NRs attached into DNA-origami molds.

References

[1] D. Mathur, I. L. Medintz, *Anal. Chem.* **2017**, *89*, 2646.
[2] S. Helmi, C. Ziegler, D. J. Kauert, R. Seidel, *Nano Lett.* **2014**, *14*, 6693.

Corresponding author email: richard.weichelt@chemie.tu-dresden.de

Nanostructured inks based on gold nanoparticles and polyelectrolytes

N. Bridonneau,[1,2,3] S. Zrig,[2,3] F. Carn [1,3]

(1) *Laboratoire Matière et Systèmes Complexes (MSC), Université Paris Diderot, Paris, UMR 7057 CNRS, Université Paris 7 Diderot, Bât. Condorcet, 10 rue Alice Domon et Léonie Duquet 75205 Paris Cedex 13, France*
(2) *Laboratoire Interfaces Traitements Organisation et DYnamique des Systèmes (ITODYS), UMR 7086 CNRS, Université Paris 7 Diderot, Paris, Bât. Lavoisier, 15 rue Jean-Antoine de Baïf, 75205 Paris Cedex 13, France*
(3) *Labex* "Science and Engineering for Advanced Materials"

Evaporating colloidal suspension leads to the formation of a variety of solid patterns, ranging from the concentric rings of a dried coffee drop to the uniform deposits of solid pigments left after paint drying. In the last decade, several groups have shown that evaporating suspensions of plasmonic nanoparticles is an efficient way toward the elaboration of nanostructured functional devices such as for instance gauge sensors,[1] substrate for Surface-Enhanced Raman Spectroscopy (SERS)[2] or diagnostic tools[3]. In spite of these achievements, the final deposited nanostructures are rather big (~µm) compared to the size of the nanoparticles, restricted to a limited number of 2D patterns, and the interparticle distance is poorly controlled, hindering the development of applications.

To increase the structural control at the nanometric scale, we developed a new method to self-assemble gold nanoparticles in bulk (3D) before deposition on model surfaces with controlled roughness and charge density. The nanostructuration relies on electrostatic interaction between negatively charged surfactants stabilizing the gold particles and ammonium functions of a polylysine-polyethyleneglycol copolymer designed on purpose.

This presentation will first present the different structures (SAXS and cryo-TEM) obtained in bulk by complexation between nanoparticles and polymers (polyelectrolytes or grafted polymers). Then, the correlation will be established between these 3D structures and the 2D patterns obtained after droplet deposition and drying as a function of the surface characteristics (sign of surface charge and charge density) and the speed of droplet deposition (µ-pipette or inkjet printer). These results will be compared to those obtained with reference individual nanoparticles.

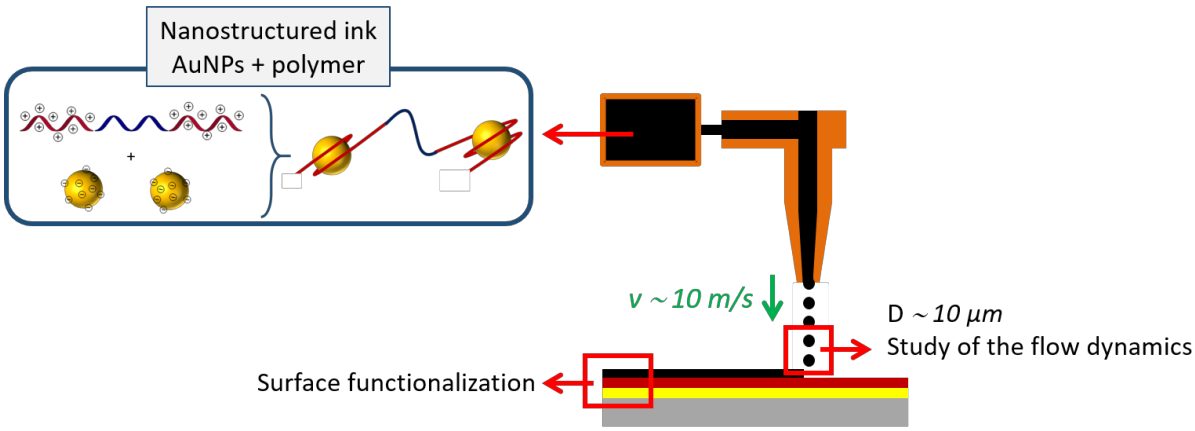


Figure 1. Deposition of nanostructured inks using the inkjet printing technique

References

1- C. Farcau, N. M. Sangeetha, H. Moreira, B. Viallet, J. Grisolia, D. Ciuculescu-Pradines, and L. Ressier, ACS Nano, **5**, 7137 (2011)
2- W. Wang, Y. Yin, Z. Tana and J. Liu, Nanoscale, **6**, 9588 (2014)
3- S. Devineau, M. Anyfantakis, L. Marichal, L. Kiger, M. Morel, S. Rudiuk and D. Baigl, J. Am. Chem. Soc., **138**, 11623 (2016)
4- R. Chen, L. Zhang, X. Li, L. Ong, Y. Gaung Soe, N. Sinsua, S. L. Gras, R. F. Tabor, X. Wang and W. Shen, ACS Sens., **2**, 1060 (2017)

Corresponding authors email: samia.zrig@univ-paris-diderot.fr & florent.carn@univ-paris-diderot.fr

Self-assembly of gold nanoparticles into structurally different tetramers using a single tetrahedral DNA template

L. Lermusiaux[1*], A. M. Funston[1]
(1) *Centre of Excellence for Exciton Science and the School of Chemistry, Monash University, VIC, 3800, Australia*

The self-assembly of metal nanocrystals on DNA scaffolds is an increasingly attracting field for the design of complex plasmonic nanostructures thanks to the recent development of DNA origami. Understanding how the presence of nano-objects may modify the DNA hybridization pathways is therefore of great importance to further synthesize nanostructures with desired geometries. In particular, it has been suggested that three-dimensional nano-assemblies could be produced by encoding tetrahedral symmetry into four thiolated DNA strands[1]. However, the spatial conformation of these assemblies in solution has not been unambiguously proven.

Here, we investigate multiple pathways to fabricate gold nanoparticle (AuNP) tetramers using a single tetrahedral DNA template (see Figure 1a). Using electrophoresis, we isolate 10 nm diameter AuNPs with a single DNA strand tethered onto their surface (named A, B, C and D in Figure 1a). Because the four strands have complementary sub-sequences, the synthesis of tetramers may include an intermediary step consisting in assembling dimers with variable interparticle distances (pathways 1 to 3). Electrophoresis is used to purify tetramers from by-products such as unreacted dimers or larger assemblies (Figure 1b). The different electrophoretic positions of the tetramer bands in the gel (five arrows at different positions) indicate that they have different hydrodynamic volumes, and therefore different morphologies[2]. This suggests that not all the tetramers synthesized are identical AuNP tetrahedra. We demonstrate that the steric hindrance introduced by the AuNPs prevents the DNA template from fully hybridizing[3]. Using steric considerations, we can identify the structures which are most likely yielded from each pathway as shown for two potential pathways in Figure 1b. Cryogenic electron microscopy experiments on the different tetramers were performed to confirm the nature of the synthesized structures and provided new insights into their behavior in solution (Figure 1c). Moreover, we show that by modifying the AuNP surface chemistry, promote their deposition as tetrahedra onto a substrate despite classical drying effects[3] (Figure 1d).

Overall, these findings will need to be considered for future origami-based AuNP self-assemblies in order to precisely control the spatial structure of discrete nanostructures. Alternatively, they could be used to develop a DNA set that would yield different AuNP assemblies with designed shapes depending on the order in which reactants are mixed.

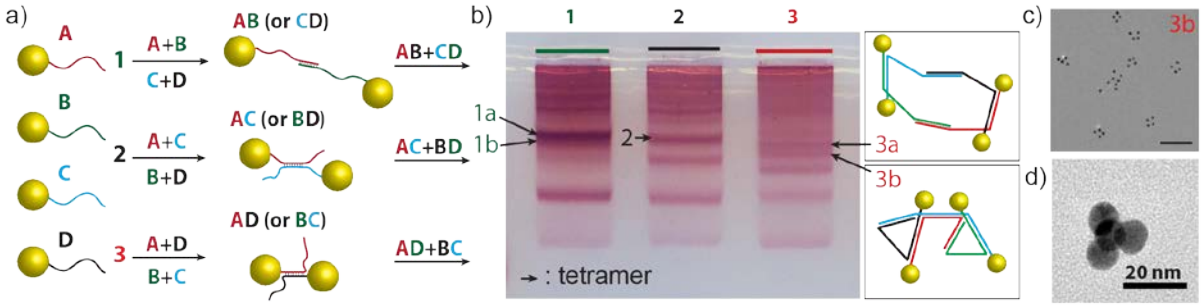


Figure 1. a) Schematic representation of three different pathways (1, 2 and 3) to fabricate AuNP tetramers using a tetrahedral DNA scaffold. b) Electrophoretic purification of five tetramer structures (1a, 1b, 2, 3a and 3b) synthesized through three different pathways. Insets: schematic presentation of structures 3a and 3b. c) Cryo-EM image of structure 3b. d) TEM image of a tetramer deposited into a 3D tetrahedron.

References

1- A. J. Mastroianni, S. A. Claridge and A. P. Alivisatos, J. Am. Chem. Soc., **131**, 8455 (2009).
2- L. Lermusiaux, A. Sereda, B. Portier, E. Larquet and S. Bidault, ACS Nano, **6,** 10992 (2012).
3- L. Lermusiaux and A. M. Funston, *in prep* (2018).

Corresponding author email: laurent.lermusiaux@monash.edu

Geometrical and Plasmonic Properties of Long-Range Ordered Pd/Au Core/Shell Nanoparticles

N. Alyabyeva[1], A. Ouvrard[1*], A. Zakaria[1], R. Lazzari[2], F. Charra[3] and B. Bourguignon[1]
(1) ISMO, CNRS, Univ. Paris-Sud, Université Paris-Saclay - Orsay (France)
(2) CNRS, UMR 7588, Institut des NanoSciences de Paris, 75005 Paris, (France)
(3) IRAMIS Institut Rayonnement Matière de Saclay, SPCSI - Gif/yvette (France).

High quality ultrathin layers of Al_2O_3 on $Ni_3Al(111)$ allow growing high density narrow size distributed nanoparticles (NPs), particularly well adapted to study small cluster reactivity [1] and that may be used as a template for nanoelectronic purposes [2]. NP plasmon response can be used to either lower down activation barrier to improve NP reactivity or enhance charge transfer to adsorbates. Combining vibrational spectroscopy with microscopy and UV/vis spectroscopy gives an original way to understand growth mechanism, geometry and interface quality and plasmonic properties of core/shell NPs.

Vibrational Sum Frequency Generation (SFG), Scanning Tunneling Microscopy and Differential Reflectance Spectroscopy (DRS) experiments have been conducted at 300 K on high-density, narrow size distributed core-shell (Pd/Au) NPs grown on ultrathin Al_2O_3 films on $Ni_3Al(111)$ done in UHV conditions [3]. STM reveals long-range ordered array of Pd NPs and that the shell thickness increase leads to a disordering of the array before coalescence, in agreement with literature [4]. The surface plasmon resonance (SPR) is observed by DRS spectroscopy for shell thicknesses larger than three monolayers (ML) and blue shifts with increasing thicknesses. Smaller the Pd core, stronger and sharper is the SPR band. NP geometry can be deduced using SFG spectroscopy by probing CO adsorption on Pd core from only few atoms to several hundred atoms per NP [5-6]. For 1 monolayer thick Au shell, a new site is observed at higher frequency and narrower bandwidth, indicating a lower adsorption energy while bridge Pd sites have disappeared. At mbar pressure, CO adsorbs on gold as expected. On the contrary for 4 and 9 ML thick Au shell, almost no CO are observed unless CO pressure is raised in the mbar range. New adsorption phase and non-reversible adsorption are observed. New sites are attributed to CO bonded on isolated Pd which migrated from the Pd core towards Au shell surface upon CO adsorption in agreement with literature [7]. Pd:Au alloy formation at the core/shell interface is limited to the first 3 ML of gold, which can be linked to DRS observations. SPR intensity is strongly affected by Pd diffusion in the shell.

The combination of STM, DRS and SFG have allowed us probing the geometry of the Pd NPs and the Pd diffusion at the core/shell interface of plasmonic Pd/Au NPs. Simulation of DRS spectra are under progress in order to extract quantitative information about NP geometry and the impact of the interface alloying on plasmonic properties.

References

1- G. Sitja *et al.*, Nano Lett. **13**, 1977 (2013).
2- S. Vlaic *et al.*, Phys. Rev. B **89**, 245402 (2014).
3- N. Alyabyeva *et al.*, Submitted to Appl. Surf. Sci.
4- A. Bailly *et al.*, J. Phys. Chem. C **121** 46 (2017).
5- A. Ouvrard *et al.,* J. Phys. Chem. C **121** 10 (2017).
6- N. Alyabyeva *et al.*, Submitted to Phys. Rev. Lett.
7- L. Delannoy *et al.*, ChemCatChem **5**, 2707 (2013).

Corresponding author email: aimeric.ouvrard@u-psud.fr

From well-defined plasmonic nanoparticles to hybrid materials for photonic and catalytic applications

C. Mendoza[1,2], B. Heinrichs[2], A. Désert[1]*, F. Lerouge[1], D. Château[1], F. Chaput[1], S. Parola[1]
(1) *Laboratoire de Chimie ENS Lyon - Université Lyon 1 - CNRS, UMR 5182, Lyon, France*
(2) *Nanomaterials, Catalysis & Electrochemistry - NCE, Department of Chemical Engineering, University of Liege, Belgium*

Our team develops research on hybrid materials devoted to optical applications, especially in the fields of optical protection, bioimaging, photocatalysis. In particular the expertise lies in the design of original molecular systems, coupled with inorganic materials like plasmonic nanostructures and the characterization of optical interactions and responses (absorption, emission, nonlinear responses…). In this context and through various studies, we will see the benefits and the way to use gold nanoparticles, from their well-controlled synthesis, and also their functionalization and incorporation in hybrid materials, to their impact on the optical and catalytic properties.

Among numerous classes of nanoparticles like spheres, hollow spheres or nanorods, we have particularly investigated gold nano-bipyramids (AuBPs) for several years.[1] Indeed, these AuBPs exhibit intense and well-defined plasmon resonance, easily tunable with the aspect ratio, and also strong localized electromagnetic field in the vicinity of the tips. Currently, our optimized synthesis method leads to well-designed AuBPs in high yield and in high concentration, with a sharp plasmon band tunable from 650 nm up to 2000 nm.[2]

We have recently developed an easy and general gold surface modification by a functional thiolated silicon polymer.[3] In addition to be an alternative to the use of surfactants or long-chain polymers in order to provide efficient colloidal stabilization in a wide range of solvent, this surface modification allows us to prepare homogeneous hybrid materials like gold-doped sol-gel silica presenting clear plasmon band. Association with various photoactive compounds have been explored and positive impact such as enhancement have been shown for photocatalytic properties of SiO_2/TiO_2 films,[4] or for non-linear optical absorption of dye-doped glasses.[5,6] Finally, we will present in particular our current efforts to synthetize core-shell AuBP@SiO_2 NPs combining with rose Bengal for catalysis based on singlet oxygen generation.

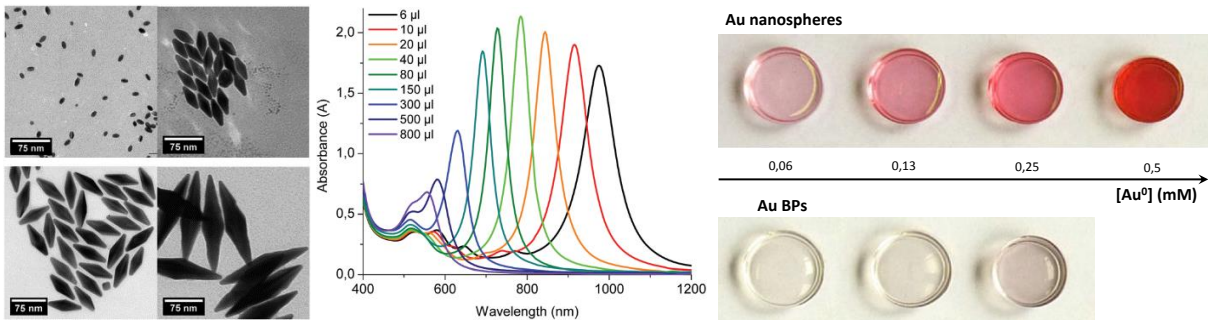


Figure - Left: TEM of bipyramids prepared with CTAB and 800, 80, 40 and 6 µl of seed suspension. Middle: Absorption spectra of the synthesized bipyramids versus the volume of seed solution added. Right: gold-doped sol-gel silica materials. (from ref. 2-3)

References

1- J.R.G. Navarro, D. Manchon, F. Lerouge, E. Cottancin, J. Lermé, C. Bonnet, F. Chaput, A. Mosset, M. Pellarin, S. Parola, *Nanotechnology* **23**, 145707, 2012.
2- D. Chateau, A. Liotta, F. Vadcard, J. R. G. Navarro, F. Chaput, J. Lermé, F. Lerouge, S. Parola, *Nanoscale* **7**, 5, 1934 (2015).
3- D. Chateau, A. Liotta, D. Gregori, F. Lerouge, F. Chaput, A. Desert, S. Parola, *Journal of Sol-Gel Science and Technology* **81**, 1, 147 (2016).
4- I. Levchuk, M. Sillanpää, C. Guillard, D. Gregori, D. Chateau, F. Chaput, F. Lerouge, S. Parola, *Journal of Catalysis* **342**, 117 (2016).
5- D. Chateau, A. Liotta, H. Lundén, F. Lerouge, F. Chaput, D. Krein, T. Cooper, C. Lopes, A.A.G El-Amay, M.Lindgren, S. Parola, *Advanced Functional Materials* **26**, 33, 6005 (2016).
6- H. Lundén, C. Lopes, M. Lindgren, A. Liotta, D. Chateau, F. Lerouge, F. Chaput, A. Désert, S. Parola, *Optical Materials* **69**, 134 (2017).

Corresponding author email: anthony.desert@ens-lyon.fr

Plasmonic properties of supported Au and Au-Pd nanoparticles: optical and structural *in situ* characterization during their growth

Yvonne Soldo-Olivier[1*], Antoine Abisset[1], Yves Garreau[2,3], Alessandro Coati[3] and Marie-Claire Saint-Lager[1]

(1) *Institut Néel (CNRS & Université Grenoble Alpes), 25 rue des Martyrs, Grenoble, France*

(2) *Matériaux et Phénomènes Quantiques, Université Denis Diderot Paris VII, Bâtiment Condorcet, Case Courrier 7021, 75205 Paris Cedex 13, France*

(3) *Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif sur Yvette Cedex, France*

Recent experiments[1,2] have shown an important increase of the catalytic activity for chemically synthesized gold or gold alloyed nanoparticles under visible light exposition. Such phenomenon has been attributed to surface plasmon resonance modes localized on nanoparticles (LSPR, local surface plasmon resonance). It is extremely relevant in the context of energy-efficient processes using solar light, in particular in order to transform visible light into chemical energy via photocatalytic reactions.

In this context, the combination of gold, known for its LSPR, with palladium, characterized by important catalytic properties, is very promising but very little is known about the plasmonic properties of Au-Pd bimetallic nanoparticles (NP). However, a deep comprehension of these LSPR-assisted processes, especially at the nano/atomic level, is a key step in order to allow large scale development of plasmon assisted photocatalysis.

In the aim of exploring the link between plasmonic properties and structure of the NPs, our approach consists in studying model systems[3], namely Au and AuxPd1-x nanoclusters deposited by molecular beam epitaxy (MBE) onto TiO2(110). For the first time, we succeeded in performing *in situ* coupled measurements of the morpho-structural and optical properties during the growth of few nanometers sized bimetallic nanoparticles. Experiments were done at SOLEIL synchrotron (France) by means of Grazing Incidence Small Angle X-ray Scattering (GISAXS), providing size, shape and inter-particle distance, Grazing Incidence X-ray Diffraction (GIXRD) for crystallographic properties and UV-Vis surface differential reflectivity spectroscopy (SDRS) for optical response.

We will firstly present the results obtained during the growth of the Au NP: the influence of the substrate and of their size on the plasmonic response will be discussed. We will then consider the influence of Pd adding, both in sequential and co-deposition for several compositions. Our study shows a great influence of palladium on the NPs growth mechanisms, as well as on their plasmonic response that critically depends on the NPs composition but also on their structure/morphology.

The presented results show the relevance of our approach in the understanding of the mechanisms underlying the plasmon assisted catalysis observed for the AuPd system[1].

References

1- S. Sarina et al., JACS **135**, 5793 (2013).
2- S. Mukerjee et al., Nano Lett. **13** 240 (2013).
3- I. Laoufi et al., J. Phys. Chem. C **4673** 115 (2011).

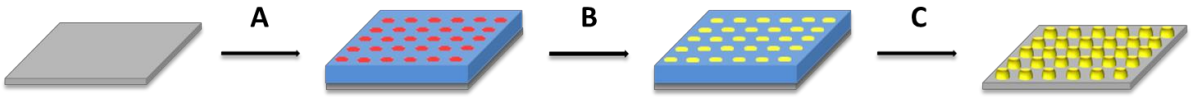
Corresponding author email: yvonne.soldo@neel.cnrs.fr

Block copolymer based nanoplasmonic surfaces

A. Alvarez-Fernandez[1,2], G. Pecastaings[2], G. Hadziioannou[2], G. Fleury[2], V. Ponsinet[1]

(1) *Centre de Recherche Paul Pascal, Univ. Bordeaux, CNRS UPR 8641, Pessac, France*
(2) *Laboratoire de Chimie des Polymères Organiques, Univ. Bordeaux, CNRS UMR 5629/ENSCBP, Pessac, Franc*

Metasurfaces have been gaining increasing attention as they demonstrate exceptional abilities for controlling the propagation of light, giving rise to properties which are not available by conventional planar and thin interfaces. They usually consist of flat arrays of optical resonators with spatially varying geometric parameters and subwavelength separation, classically fabricated by lithography techniques such as photolithography or electron-beam lithography. We show in this presentation that block copolymer self-assembly give access to a straightforward and versatile nanofabrication method for this type of structures.



Scheme 1: General diagram of the fabrication process, A) Block copolymer self-assembly, B) Selectively gold salt incorporation C) Oxygen plasma treatment to reduce the gold salt to metallic gold

We present a large variety of metasurfaces (Figure 1), from simple metallic hexagonal dots or continuous metallic lines to more complex structures such us raspberry-like bimetallic nanoclusters, all produced by a simple process involving self-assembled thin films of different molecular weight poly(styrene)-b-poly(2-vinyl pyridine) (PS-b-P2VP) copolymers, synthetized by living anionic polymerization : thin polymer films of chosen morphology are first deposited on the chosen substrate, then the metallic precursor is deposited and selectively incorporated into the P2VP domains and then reduced in a subsequent step by O_2 RIE (Schema 1). Grazing-Incidence Small Angle X-ray Scattering, Atomic Force Microscopy, Scanning Electron Microscopy, X-ray Photoelectron Spectrometry, and Kelvin Probe Force Microscopy have been used to follow each step of the fabrication process. Besides, the optical properties of the nanostructured films, strongly affected by their plasmon resonances, are studied by variable-angle spectroscopic ellipsometry.

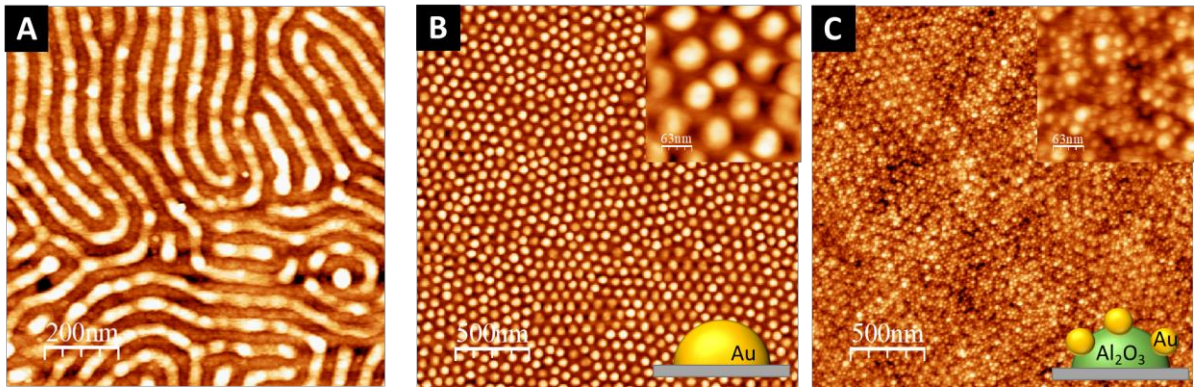


Figure 1. AFM micrographs of gold plasmonic metasurfaces obtained using PS-b-P2VP as a template (A) Continuous gold lines (bar=200nm) (B) Gold dots with hexagonal order (bar=500nm, inset bar=63nm) and (C) Raspberry-like bimetallic nanoclusters also with hexagonal order (bar=500nm, inset bar=63nm)

This work was supported by the LabEx AMADEus (ANR-10-LABX-42) in the framework of IdEx Bordeaux (ANR-10-IDEX-03-02), France.

Corresponding author email: falvarez@crpp-bordeaux.cnrs.fr

Geometry Dependent Plasmon Resonance Mode Evolution in Crystalline, Faceted Gold Nanotriangle Dimers

Mayevsky A.D. [1*], Funston A.M. [1]

[1] *ARC Centre of Excellence for Exciton Science and School of Chemistry, Monash University, Clayton 3800, Australia*

The localised surface plasmon resonances of two metallic nanoparticles in close proximity can interact with each other to form a coupled plasmon mode. This type of interaction results in large electric field enhancements in the interparticle space, and this kind of enhancement increases proportionally to reduction in interparticle separation[1]. Assembly of chemically grown nanoparticles allows for a minimization of interparticle separation as the lower distance limit is set by primary protecting ligand contact. Furthermore, unlike fabrication techniques which necessarily cause morphological changes and modify optical properties[2], assembly retains the structural integrity of the nanoparticles.

We report the scattering spectra for a series of gold nanotriangle dimers with varying geometries[3] (see Fig. 1a). The gold nanotriangles were chemically grown and have unique three-dimensional morphology. A symmetrical dimer assembled into a bowtie-like arrangement has a longitudinal mode at 893 nm (see Fig. 1b) this is a 294 nm red-shift relative to a monomer nanotriangle of equivalent size. Given the extremely large red-shift and three-dimensional morphology of the component nanotriangles, it is likely that this bowtie exhibits a large electric field enhancement and localisation in the in interparticle space. Additionally, by varying the edge-edge offset of a nanotriangle dimer, it is possible to tune the longitudinal plasmon resonance within a 170 nm range (see Fig. 1c), and this simultaneously affects the energy of the transverse mode (see Fig. 1d).

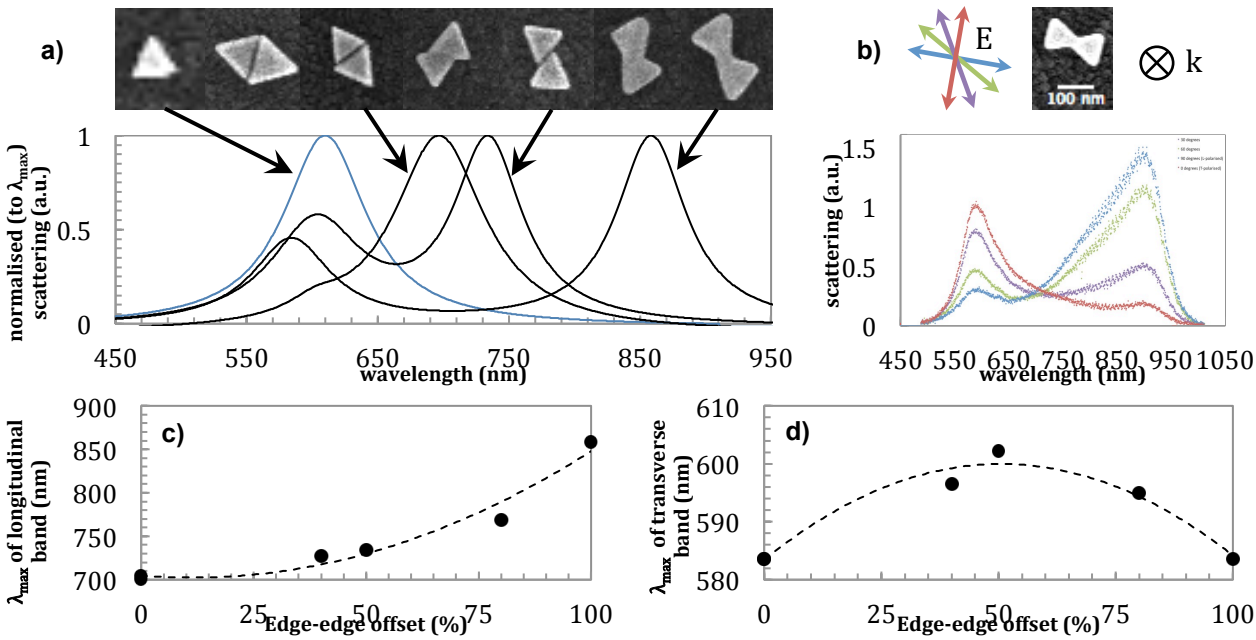


Figure 1: (a) SEM images and Lorentzian fits of single particle scattering spectra for a series of nanotriangle dimers. All nanotriangles have an edge length of 80nm. (b) Lorentzian fits of polarisation resolved single particle spectra for the bowtie-arranged dimer indicated. (c & d) Mode evolution of the longitudinal (c) and transverse (d) bands for nanotriangle dimers with respect to edge-edge offset.

References:

[1] Dodson S, Haggui M, Bachelot R, Plain J, Li S, Xiong Q. Optimizing Electromagnetic Hotspots in Plasmonic Bowtie Nanoantennae. J Phys Chem Lett 2013;4:496–501. doi:10.1021/jz302018x.

[2] Huang J-S, Callegari V, Geisler P, Brüning C, Kern J, Prangsma JC, et al. Atomically flat single-crystalline gold nanostructures for plasmonic nanocircuitry. Nat Commun 2010;1:150. doi:10.1038/ncomms1143.

[3] Mayevsky AD, Funston AM. Draft in preparation.

Corresponding author email: ari.mayevsky@monash.edu

New Advances in Chemistry of Hybrid Plasmonic Nanoparticles

I. Kherbouche[1,2], M. Nguyen[2], I. Tijunelyte[1,3], N. Lidgi-Guigui[3], M. Lamy de la Chapelle[3], A. Lamouri[2], G. Lévi[2], J. Aubard[2], A. Chevillot-Biraud[2], S. Lau-Truong[2], N. Felidj[2], C. Mangeney[1]

(1) University Paris 05, Lab Chim & Biochim Pharmacolog & Toxicol, 75006 Paris, (France)
(2) University Paris Diderot, ITODYS, 75013 Paris (France)
(3) CSPBAT, Université Paris 13, 93430 Villetaneuse (France)

In this talk, we present the design of hybrid plasmonic nanostructures, combining gold nanoparticles and functional polymers (smart, reactive and molecularly imprinted polymers). We will first describe an original strategy for the regioselective functionalization of gold nanoparticles, based on a combination of photo-induced plasmon excitation and aryl diazonium salt chemistry[1-4]. The aryl films derived from diazonium salts are specifically grafted in areas of maximum near field enhancement, as confirmed by numerical calculation based on the discrete dipole approximation method - DDA. This emerging field at the interface between plasmonics and surface functionnalization offer exciting perspectives for the nanoscale confinement of functional layers on surface, of particular interest for molecular sensing or nanooptics applications. We will then describe the coupling between plasmonic nanostructures and thermosensitive polymers to yield smart nanosystems for sensing and active plasmonic applications[5,6] (see Figure 1). The grafting of molecularly imprinted polymer shells is also shown to provide optical nanosensors enabling the direct, label-free detection of various kinds of molecules, such as folic acid and paracetamol[7,8]. The combination of plasmonic nanostructures and polymers therefore offers promising outlook to merge multiple functions at the nanometer scale. It allows integrating building materials of various chemical natures into the same active plasmonic platform to provide smart devices with unprecedented performances..

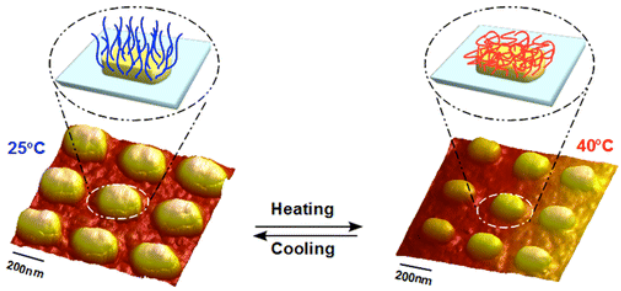


Figure 1. Regular array of gold nanoparticles, elaborated by electron beam lithography, and functionalized by smart thermoresponsive polymer brushes.

References

1- I. Tijunelyte, I. Kherbouche, S. Gam-Derouich, M. Nguyen, N. Lidgi-Guigui, M. Lamy de la Chapelle, A. Lamouri, G. Lévi, J. Aubard, A. Chevillot-Biraud, C. Mangeney, N. Felidj, *Nanoscale Horizon*, **3**, 53 (2018).
2- M. Nguyen, I. Kherbouche, S. Gam-Derouich, I. Ragheb, S. Lau-Truong, A. Lamouri, G. Levi, J. Aubard, P. Decorse, N. Felidj, C. Mangeney, Chem. Comm., **53**, 11364 (2017).
3- V-Q Nguyen, Y Ai, P Martin, J-C Lacroix, ACS Omega, **2**, 1947 (2017).
4- M. Nguyen, A. Lamouri, C. Salameh, G. Levi, J. Grand, L. Boubekeur-Lecaque, C. Mangeney, N. Felidj, Nanoscale, **8**, 8633 (2016).
5- M. Nguyen, N. Felidj, C. Mangeney, Chem. Mater., **28**, 3564 (2016).
6- M. Nguyen, X. Sun, E. Lacaze, P. Winkler, A. Hoheneau, J. Krenn, C. Bourdillon, A. Lamouri, J. Grand, G. Lévi, L. Boubekeur-Lecaque, C. Mangeney, N. Felidj, ACS Photonics, **2**, 1199 (2015).
7- R. Ahmad, N. Félidj, L. Boubekeur-Lecaque, S. Lau-Truong, S. Gam-Derouich, P. Decorse, A. Lamouri, C. Mangeney, Chem. Comm., **51**, 9678 (2015).
8- R. Ahmad, N. Griffete, A. Lamouri, N. Félidj, M.M. Chehimi, C. Mangeney, Chem. Mater, **27**, 5464–5478 (2015).

Corresponding author email: claire.mangeney@parisdescartes.fr

NEW SYNTHESIS OF GOLD NANOPARTICLES USING N-HETEROCYCLIC CARBENE BORANES

L. Hippolyte[1,2*], N. Bridonneau[1], D. Mercier[3], D. Portehault[1], M. Desage-El Murr[2], L. Fensterbank[2], C. Chanéac[1], F. Ribot[1]

(1) *Sorbonne Université, CNRS, Collège de France, Laboratoire Chimie de la Matière Condensée de Paris, LCMCP, F-75005 Paris, France*

(2) *Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, IPCM, F-75005 Paris, France*

(3) *PSL Research University, Chimie ParisTech, CNRS, Institut de Recherche de Chimie Paris, IRCP, F-75005 Paris, France*

Gold nanoparticles have been known for a long time and have found applications in many fields such as medicine, optics, electronics or catalysis. Their most common syntheses generally require three components: a gold precursor, a reducing agent and a stabilizing ligand.

N-Heterocyclic carbenes (NHCs) are persistent carbenes with highly tunable structures. In recent years their chemistry has blossomed and they have shown a strong affinity for a wide range of metals[1]. In the case of gold, this affinity has been shown to be higher than with thiols[2].

A few studies have shown the possibility to use NHCs to stabilize gold nanoparticles[3-5], starting from NHC-gold complexes, (benz)imidazolium-gold complexes or by exchanging a sacrificial ligand with free NHCs.

NHCs, which are Lewis bases, can also form with borane (Lewis acid) stable adducts[6], which exhibit reducing properties. NHC-boranes were thus explored as "2-in-1" reagents, ie. reducing agent and source of stabilizing ligands, in the synthesis of gold nanoparticles.

A synthesis of NHCs stabilized gold nanoparticles is reported for the first time from NHC-boranes and $AuClSMe_2$ as gold precursor[7]. XPS analysis confirms the presence of NHCs as surface ligands. Varying the reaction conditions allows tuning the average nanoparticle size in the range 5-10 nm.

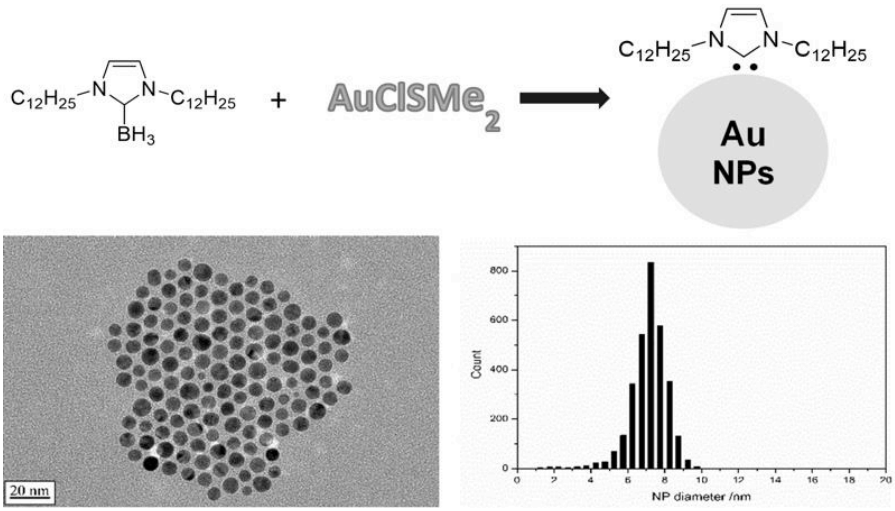


Figure 1. Scheme of the nanoparticles synthesis, TEM image of obtained nanoparticles and corresponding size distribution

References

1- M. N. Hopkinson, C. Richter, M. Schedler *et al.*, Nature **510**, 485 (2014).
2- C. M. Crudden, J.H. Horton, I.I. Ebralidze *et al.,* Nat. Chem. **6**, 409 (2014); C. M. Crudden, J.H. Horton, M.R. Narouz *et al.,* Nat. Commun. **7**, 12654 (2016).
3- J. Vignolle, T.D. Tilley, Chem. Commun. 7230 (2009); K. Salorinne, R. W. Y. Man, C.-H. Li et al., Angew. Chem., **129**, 6294 (2017).
4- E.C. Hurst, K. Wilson, I.J.S. Fairlamb *et al.*, New J. Chem. **33**, 1837 (2009).
5- C.J. Serpell, J. Cookson, A.L. Thompson *et al.*, Dalton Trans **42**, 1385 (2013); X. Ling, S. Roland, M.-P. Pileni, Chem. Mater. **27**, 414 (2015).
6- D.P. Curran, A. Solovyev, M. Makhlouf Brahmi *et al.*, Angew. Chem. Int. Ed. **50**, 10294 (2011).
7- L. Hippolyte, N. Bridonneau, F. Ribot, *et al.*, manuscript in preparation

Corresponding author email: laura.hippolyte@upmc.fr

Tailoring the shape of core-shell Au-Ag nanoparticles for SERS

I. Haidar[1], A. Chevillot-Biraud, S. Lau-Truong[1], N. Félidj[1], L. Boubekeur-Lecaque[1*]
(1) *Laboratoire ITODYS UMR 7086, Université Paris Diderot, Sorbonne Paris Cité, 15 rue J-A de Baïf, 75205 Paris Cedex 13, France*

The shape and size control of metal nanoparticle at the nanoscale is a crucial step in the development of diverse applications ranging from catalysis to plasmonics and surface-enhanced Raman spectroscopy (SERS). Among the nanomaterials reported, Au and Ag nanoparticles are the most popular and their geometry-dependent optical properties have been extensively studied. In particular, the seed-mediated growth method proved to be a very powerful route to fine-tune the size, morphology and elemental composition of the nanoparticle by simply reducing additional metal ions on pre-existing metal seeds. The formation of core-shell hybrid nanostructures where gold nanorods (Au NRs) serve as template for the overgrowth of Pd, Pt and Ag shell has been described. [1] Specifically, silver-coated Au nanorods of various shapes have been synthesized by adjusting the conditions (ligand, additives, solvent, temperature, etching…). Still, the exact mechanism of Ag anisotropic deposition for some specific shapes remains to be unraveled. [2]

We present a novel method for the synthesis of a series of anisotropic core-shell Au@Ag of various shapes starting wih the same AuNR template. The control of Ag overgrowth on single crystalline gold nanorods was mainly tailored by organic ligand (additive) added in the growth medium. [3] The combination of UV-visible extinction spectroscopy and SEM provided information about morphology at each step of the overgrowth process and transient morphological changes. Surfactant halide counter-ion exchange on the gold surface and coordination of the organic additive were clearly revealed by SERS and XPS. This study has contributed to establishing the key parameters that govern the overgrowth mechanism.

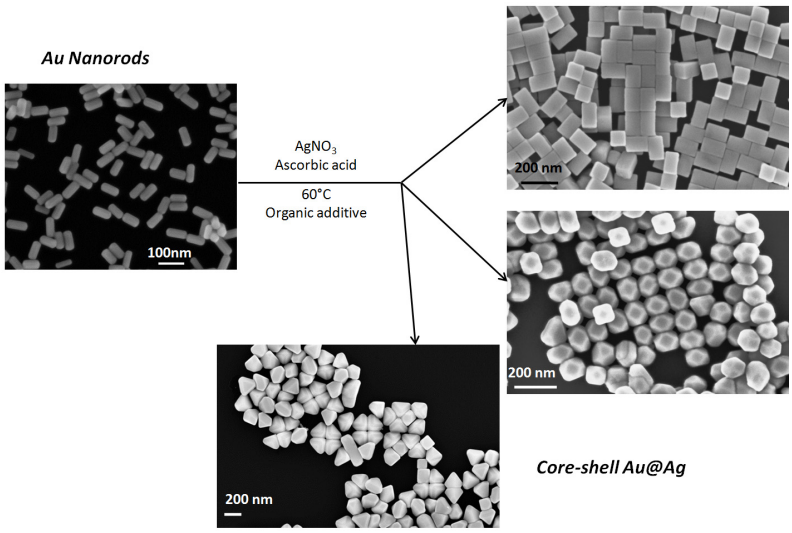


Figure 1. Representative SEM micrographs of various shapes of core-shell Au@Ag designed by silver overgrowth on the same gold nanorods template.

The core-shell Au@Ag nanoparticles obtained via this synthetic strategy tend to self-assemble on large area on solid substrate (silicon, or glass). Through a bottom-up approach, these densely packed nanoparticle films showed very promising SERS-active substrates in terms of homogeneity, stability over time and overall cost-effectiveness.

References

1- S. Hou, X. Hu, T. Wen, W. Liu, and X. Wu, Adv. Mat. **25**, 3857 (2013).
2- S. Gomez-Graña, B. Goris, T. Altantzis, et. al, J. Phys. Chem. Lett., **4**, 2209 (2013)
3- Boubekeur-Lecaque, L.; Haidar, I.; Félidj, N.; Neuville, D. R.; FR Patent 1659934, 2016, submitted

Corresponding author email: leila.boubekeur@univ-paris-diderot.fr

THERMODYNAMIC EQUILIBRIUM AND MAXIMUM YIELD IN COLLOIDAL NANOCRYSTALS SYNTHESIS

E. A. Slejko[1*], V. Lughi[1]
(1) *DIA – Department of Engineering and Architecture, University of Trieste, Trieste, Italy*

Intensive production of colloidal nanocrystals is becoming increasingly essential considering the high amount of nanomaterial required in several applications (catalysis, biomedical and therapeutic, optoelectronics, etc.), and the growing spreading of nanocrystal-based devices. Therefore, the concept of synthesis yield is of paramount importance for the large-scale fabrication of colloidal nanostructures. A modification of the classical nucleation theory is proposed to model the size evolution and to identify an equilibrium (final) size of the nanocrystals, taking into account the consumption of precursor during nanocrystal growth in solution, a common situation for all batch syntheses of nanostructures. The modification consists on the addition of a new supersaturation term in the potential equation, whose curve now displays a minimum when the system has reached thermodynamic equilibrium and the reaction yield exhibits its maximum value (Figure 1). A specific nanocrystal size is associated to the minimum: it represents the maximum size crystals could reach under the specified set of synthetic conditions (without considering other aging processes like, for example, Ostwald ripening). Assessment of the model has been performed by comparing simulated results to experimental data found in literature. The modified nucleation theory, with its equilibrium size feature, represents a valuable tool for the efficient design of scalable colloidal nanocrystal syntheses.

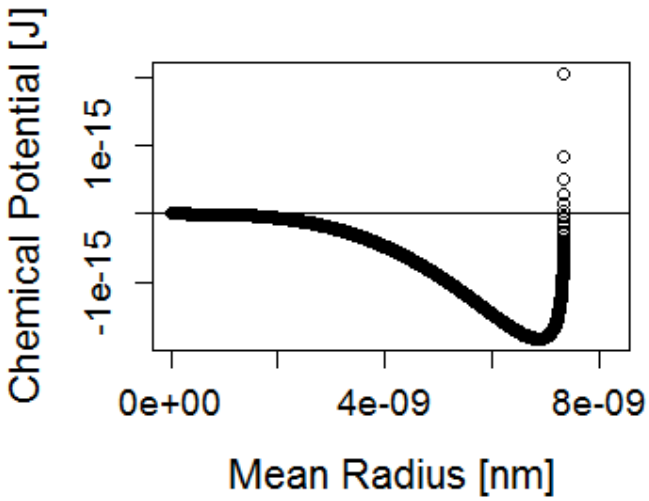


Figure 1. Exemplificative chemical potential curve for a closed system

Corresponding author email: emanuelealberto.slejko@phd.units.it

Colloidal Alchemy: Conversion of Polystyrene Nanoclusters into Gold

V. Many[1,2], J. Majimel[1], G. Drisko[1], S. Mornet[1], P. Barois[2], A. Baron[2], S. Ravaine[2], E. Duguet[1], M. Treguer-Delapierre[1]

(1) ICMCB-CNRS, UPR 9048, France, Pessac
(2) CRPP-CNRS, UPR9048, France, Pessac

Isotropic plasmonic clusters consisting of a controlled number of gold satellites around a silica core were fabricated by using the concept of patchy particles. The versatile chemical approach that we have developed offers the possibility to produce Platonic solids, such as tetrapods (tetrahedra), hexapods (octahedra) and dodecapods (icosahedra) like nanoclusters on a large scale i.e. in gram quantities. These plasmonic clusters, in particular the dodecapods ones, have unique plasmonic properties and may be suitable for many applications in the field of optics, biosensing, photonics. These nano-objects have indeed extraordinary optical responses including magnetic response and metafluid behavior.

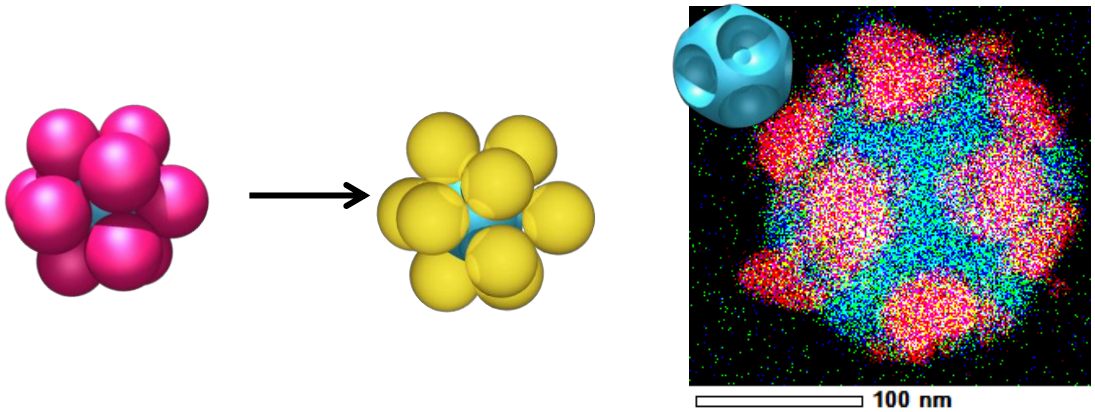


Figure 1: EDX image of well-defined SiO_2/Au dodecapods

References

C. Chomette, M. Treguer-Delapierre, S. Ravaine, E. Duguet and coworkers, ChemNanoMat, 2017, 3,160 –163

Corresponding author email: veronique.many@icmcb.cnrs.fr

Assembly of Janus gold-silica plasmonic particles

U. Martino[1*], S. Lau-Truong[1], N. Félidj[1], L. Boubekeur-Lecaque[1]
(1) *Laboratoire ITODYS UMR 7086, Université Paris Diderot, Sorbonne Paris Cité, 15 rue J-A de Baïf, 75205 Paris Cedex 13, France*

As researchers began to investigate the Surface enhanced Raman scattering (SERS) effect using colloidal nanoparticles (NPs), it soon became apparent that the extremely intense SERS signals originate mainly from aggregated NPs.[1]

Our group reported on a simple and efficient strategy to assemble gold nanorods (AuNRs) into long-term stable dimers. [2] Both experimental (SERS) and theoretical (DDA calculations) studies of the near-field characteristics revealed two-orders of magnitude increase of the SERS enhancement factor for the dimers as compared to isolated AuNRs. [3] The removal of isolated AuNRs (unavoidable by-products) from aggregates is particularly desirable given that AuNRs dimers have been clearly shown to provide much higher enhancement. However, important issues related to the purification of the final colloidal assembly containing AuNRs dimers and monomers remain unresolved for solution-based SERS. In this work, a bottom-up approach has been adopted for addressing these critical issues in solution-based SERS experiments and advancing the search for an optimal SERS substrate.

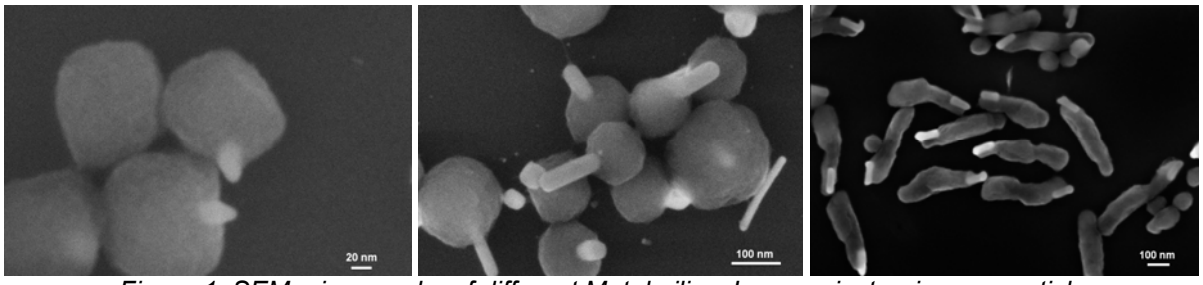


Figure 1. SEM micrographs of different Metal-silica Janus anisotropic nanoparticles

The control of the number of AuNRs involved in each cluster and their relative arrangement would rely on the partial and regioselective coating of GNRs tips with a mesoporous silica layer (Au@SiO_2 Janus nanorods). We explored different synthetic strategies to obtain anisotropic Janus particles which are the building blocks for assembly. Besides thermal and colloidal stability, mesoporous silica coating of nanoparticles imparts other notable advantages due to its porosity which can be exploited for drug or dye loading.

References

1- Schlücker, S., Surface-Enhanced Raman Spectroscopy: Concepts and Chemical Applications. *Angew. Chem., Int. Ed.*, ***53***, 4756 (2014).
2- Haidar, I.; Aubard, J.; Levi, G.; Lau-Truong, S.; Mouton, L.; Neuville, D. R.; Felidj, N.; Boubekeur-Lecaque, L., Design of Stable Plasmonic Dimers in Solution: Importance of Nanorods Aging and Acidic Medium. *J. Phys. Chem. C*, ***119***, 23149 (2015).
3- Haidar, I.; Aubard, J.; Levi, G.; Lau-Truong, S.; Mouton, L.; Neuville, D. R.; Felidj, N.; Boubekeur-Lecaque, L., Highly stable silica-coated gold nanorods dimers for solution-based SERS, PCCP, **18**, 32272 (2016)

Corresponding author email: martino.umberto@etu.univ-paris-diderot.fr

Novel synthesis and characterization of doxycycline-loaded gold nanoparticles. The golden doxycycline for antibacterial applications

M.Ben Haddada[1]*, K.Jeannot [2], M. Lamy de la Chapelle [3,4], J.Spadavecchia[1]
(1) CNRS, UMR 7244, CSPBAT, Laboratoire de Chimie, Structures et Propriétés de Biomateriaux et d'Agents Therapeutiques, Université Paris 13, Sorbonne Paris Cité, Bobigny, France
(2) Centre National de Référence de la Résistance aux Antibiotiques, Centre Hospitalier Régional Universitaire, Besançon, France
(3) Institut des Molécules et Matériaux du Mans (IMMM - UMR CNRS 6283), Le Mans Université, Le Mans, France
(4) Southwest Hospital, Third Military Medical University, Chongqing, China

Doxycycline (DOXY) is a tetracycline antibiotic with a potent antibacterial activity against a wide variety of bacteria[1,2]. However, poor cellular penetration limits its use for the treatment of infectious disease caused by intracellular pathogens. One potential strategy to overcome this problem is the use of nanotechnology that can help to easily target the intracellular sites of infection. Their large surface area to volume ratio, biocompatibility and bioconjugation possibilities, inorganic nanoparticles are promising candidates for delivering large amounts of antibiotics without changing their activity[3,4]. The combination of antibiotics to inorganic nanoparticles might enhance their antimicrobial effectiveness against multidrug resistant bacteria [5-7].

In this study, we report for the first time the synthesis, physico-chemical characterization of DOXY-complex–gold-COOH-terminated PEG-coated nanoparticles (DOXY-PEG-AuNPs) according to two synthesis schemas. The first synthetic approach (DOX IN–PEG–AuNPs) consists in four steps: Complexation between doxycycline (DOXY) and tetrachouric acid ($HAuCl_4$) to form gold clusters; adsorption of COOH-terminated PEG molecules (PEG) onto DOXY-Au complex; reduction of metal ions in that vicinity, growth of gold particles and colloidal stabilization. The second is the synthesis of polymer-modified AuNPs loaded with DOXY by covalent linkage, referred as DOXY ON-PEG-AuNPs.

The obtained nanoparticles were fully characterized by transmission electron microscopy (TEM), using dynamic light scattering (DLS), zeta-potential, UV-Vis and Raman spectroscopy.

The stability and sustained activity of the drug loaded nanoparticles was seen in the above bacterial culture and the results were compared with the native form of the drug. This combined therapeutic agent showed greater bactericidal activity against E.coli and P. aeruginosa. Tests were also performed on several P.aeruginosa strains harboring several resistance mechanisms to antibiotics. The minimal inhibition concentration (MIC) values showed significant reduction for the DOXY-conjugated AuNPs compared to the free DOXY.

Furthermore, the interactions among DOXY, PEG, and Au (III) ions in DOX IN–PEG–AuNPs differed significantly from DOXY ON–PEG–AuNPs. The bacteriological experiments indeed demonstrated that such differences strongly influenced the anti-bacterial potential of AuNPs.

References

1- J. N. Doxycycline revisited, Arch Intern Med **157**, 1421(1997).
2- C. B. Pharmacodynamics of doxycycline, Clin Microbiol Infect **6**, 270(2001).
3- R.A. Antibiotic mediated synthesis of gold nanoparticles with potent antimicrobial activity and their application in antimicrobial coatings. J. Mater. Chem **20**, 6789(2010).
4- C.N. Synergetic effects of doxycycline-loaded chitosan nanoparticles for improving drug delivery and efficacy. International Journal of Nanomedicine **7**, 2411(2012).
5- T.R. Ciprofloxacin-Protected Gold Nanoparticles. Langmuir **20**, 1909(2004).
6- M.R. Antibacterial activity of doxycycline-loaded nanoparticles. Methods Enzymol **509**, 61(2012).
7- F. A. Synthesis and characterization of core-shell bimetallic nanoparticles for synergistic antimicrobial effect studies in combination with doxycycline on burn specific pathogens. J. Photochem. Photobiol. B: Biol **169**, 21(2017).

Corresponding author email: maroua.benhaddada@gmail.com

The Gold Ampicilin Interface At the Nanoscale : A Numerical Simulation Study

X. Fenouillet[1*], M. Benoit[1*], N. Tarrat[1*]
(1) *CEMES, Université de Toulouse, CNRS, 29 rue Jeanne Marvig, 31055 Toulouse, France*

The accelerating emergence of multi-drug-resistant (MDR) pathogenic microbia has become a significant global public health threat [1]. The World Health Organization estimates 10 millions death a year due to these MDR [2]. Since the discovery of new antibiotic family stopped in the 90's, new methods to fight this increasing threat have to be found. Very recently, it has been shown that gold nanoparticles (AuNPs) conjugated with antibiotics are potential bactericidal agents with unique properties that subverted antibiotic resistance mechanisms of MDR bacteria. Furthermore, resistance to antibiotics-conjugated gold nanoparticles develops significantly more slowly than to the last commercial molecules generation [3].

The ampicillin molecule ($C_{16}H_{19}N_3O_4S$), belonging to the β-lactam family, is a broad spectrum antibiotic used to treat a lot of different diseases. It acts by inhibiting the creation of the bacterial cell wall, thus leading to lysis. However, its overuse as a prevention agent in fields like livestock battery led to a huge decrease in its efficiency. Bhattacharya and al. [4] have conjugated AuNPs with several antibiotics including ampicillin. The results showed that the AuNP-ampicillin complex exhibits outstanding properties. It is stable (UV, heat and prolonged storage), allowing for transportation and industrialization. It is also more efficient than the free antibiotic in the fight against bacteria. A. N. Brown and al [5] also shown that such complex is able to kill MDR while the free ampicillin molecule is inefficient.

To rationalize and control the stability of such promising hybrid systems, a deep understanding of these complexes at the atomic scale is essential. Using numerical simulations (DFT and ab initio Molecular Dynamics), we have investigated the structure of the interface between the ampicillin antibiotics and three flat gold facets Au(111), Au(110) and Au(100) for different antibiotics coverage (from single molecule to auto-organization). These calculations indicate that the adsorption of a single ampicillin on these facets goes through multiple partially covalent bonding, the corresponding large adsorption energies explaining the stability of the AuNP/ampicillin nanoconjugates [6]. Moreover, these calculations have shown that the grafted antibiotic has a constrained spatial orientation which could be very favorable towards the antibacterial activity of these hybrid systems. When increasing the coverage, hydrogen bonds and van der Waals dispersion forces play an important role in the stabilization of the whole system. At high coverage, a possible auto-organization of the ampicillin molecules on the AuNP surfaces can be found, without loss of the favorable orientation of the antibiotics active site.

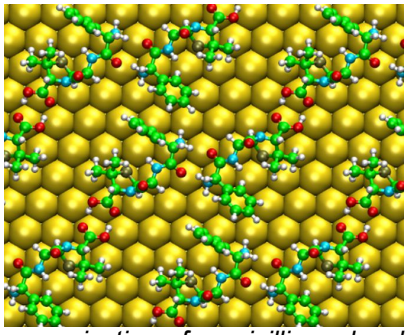


Figure 1. Auto-organization of ampicillin molecules on Au(111)

References

1- H. H. Chang *et al.*, Microbiol. Mol. Biol. Rev. **79**, 101 (2015).
2- WHO Antimicrobial resistance: global report on surveillance 2014 http://www.who.int/antimicrobial-resistance/publications/surveillancereport/en/ (2014).
3- J. Bresee *et al.*, JACS **136**, 5295 (2014).
4- B. Saha *et al.*, Nanoscale Res. Lett. **2**, 614 (2007). D. Bhattacharya *et al.*, J. Nanosci. Nanotechnol. **2**, 14 (2012).
5- A. N. Brown *et al.*, Appl. Environ. Microbiol. **78**, 2768 (2012).
6- N. Tarrat *et al.*, Nanoscale **7**, 14515 (2015).

Corresponding author email: xavier.fenouillet@cemes.fr magali.benoit@cemes.fr nathalie.tarrat@cemes.fr

Understanding the role of gold in production of ordered protein assemblies

K. Majsterkiewicz[1*], J.G. Heddle[1]
(1) *Malopolska Centre of Biotechnology, Jagiellonian University, Krakow, Poland*

The unusual properties of gold nanoparticles (GNPs) has resulted in them gaining considerable interest in a number of fields including bionanotechnology, mainly due to easy surface functionalization which can enable connection with a wide range of biological molecules, e.g. proteins and peptides. This has led to the development of delivery systems or sensing probes[1,2]. However, many questions still remain related to GNP interaction with living systems and biological molecules: A number of studies have shown that proteins can interact with GNPs forming a corona[3,4], which is structured but not highly-ordered. In contrast, we have shown interaction of a protein with GNPs resulting in ordered superstructure formation. Specifically, we showed that the protein TRAP, in presence of gold does not simply stochastically bind or form a corona, but instead forms an ordered protein cage[5,6]. The precise role of gold in this reaction is still unclear: does it act as a catalyst, a template or a linker? In the light of recent studies, we now have a clearer understanding of the function of gold in protein-cage formation and can go some way to answering these questions. This understanding along with mechanistic implications will be discussed.

References

1. Li, X. *et al.* Enhancement of cell recognition in vitro by dual-ligand cancer targeting gold nanoparticles. *Biomaterials* **32,** 2540–2545 (2011).
2. Thaxton, C. S. *et al.* Nanoparticle-based bio-barcode assay redefines ‘undetectable’ PSA and biochemical recurrence after radical prostatectomy. *Proc. Natl. Acad. Sci.* **106,** 18437–18442 (2009).
3. Cedervall, T. *et al.* Understanding the nanoparticle-protein corona using methods to quantify exchange rates and affinities of proteins for nanoparticles. *Proc. Natl. Acad. Sci.* **104,** 2050–2055 (2007).
4. Charbgoo, F. *et al.* Gold nanoparticle should understand protein corona for being a clinical nanomaterial. *J. Control. Release* **272,** 39–53 (2018).
5. Malay, A. D. *et al.* Gold Nanoparticle-Induced Formation of Artificial Protein Capsids. *Nano Lett.* **12,** 2056–2059 (2012).
6. Imamura, M. *et al.* Probing structural dynamics of an artificial protein cage using high-speed atomic force microscopy. *Nano Lett.* **15,** 1331–1335 (2015).

Corresponding author email: karolina.majsterkiewicz@uj.edu.pl

Stabilization of Au Monatomic-High Islands on the (2×2)-Nad Reconstructed Surface of Wurtzite AlN(0001)

Benoit Eydoux[1,2], Bulent Baris[1], Hassan Khoussa[1,3], Olivier Guillermet[1,2], Sébastien Gauthier[1], Xavier Bouju[1] and David Martrou[1]

(1) *Centre d'élaboration de matériaux et d'études structurales, CEMES-CNRS, UPR 8011, Nanosciences Group, 29 rue Jeanne Marvig, F-31055 Toulouse, France*
(2) *Université Toulouse III, UPS, 118 route de Narbonne, F-31062 Toulouse, France*
(3) *Laboratoire LSMC, Université d'Oran 1 Ahmed Ben Bella, 31100 Oran, Algeria*

RHEED spectra and low temperature NC-AFM images demonstrate that Au grows on the AlN(0001) (2×2)-N_{ad} reconstructed surface as large (>100 nm) monolayer islands that form moiré patterns [1]. These experimental data allow us to build atomic models that are used as input for first-principles DFT calculations. These calculations show that the hexagonal Au adlayer interacts locally with the substrate via the acceptor and donor sites existing on the (2×2)-N_{ad} reconstructed surface [2]. These interactions lead to local distortions of the hexagonal layer. Au adsorption is accompanied
(i) by a global vertical charge transfer from the AlN substrate, that fulfills the electrostatic stability criterion for a polar surface,
(ii) by lateral charge transfers mediated by the reaction of Au with the acceptor and the donor sites of the polar substrate.

The stabilization of the monolayer is the consequence of these two mechanisms that lead to energy gains of electrostatic and chemical origin. This study rationalizes the physico-chemical effects associated with the adsorption of metallic islands on a polar substrate with a nonstoichiometric reconstructed surface and opens routes for the fabrication of metallic pads particularly interesting in the context of molecular electronics. These 2D metallic pads can also be the seeds for the growth of thick 2D gold electrodes. Such electrodes with a controlled metal-semiconductor interface could improve the reliability of the nitride active devices.

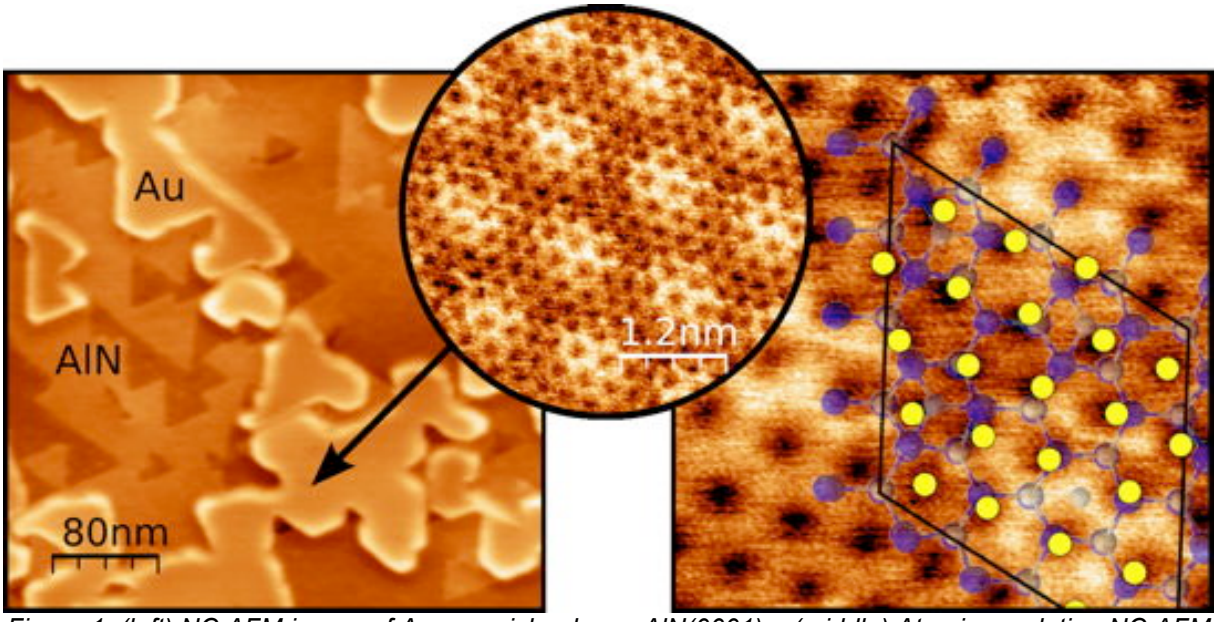


Figure 1. (left) NC AFM image of Au nano-islands on AlN(0001) ; (middle) Atomic resolution NC AFM image obtained at low temperature (5K) showing the moiré pattern formed by the Au monolayer; (right) Superposition of the model calculated by DFT (yellow : Au atom , violet : Al atom, grey : N atom) on the experimental NC-AFM image.

References
1- B. Eydoux *et al.* , Phys. Rev. Applied **8**, 044002 (2017).
2- F. Chaumeton *et al.*, Phys. Rev. B **94**, 165305 (2016).

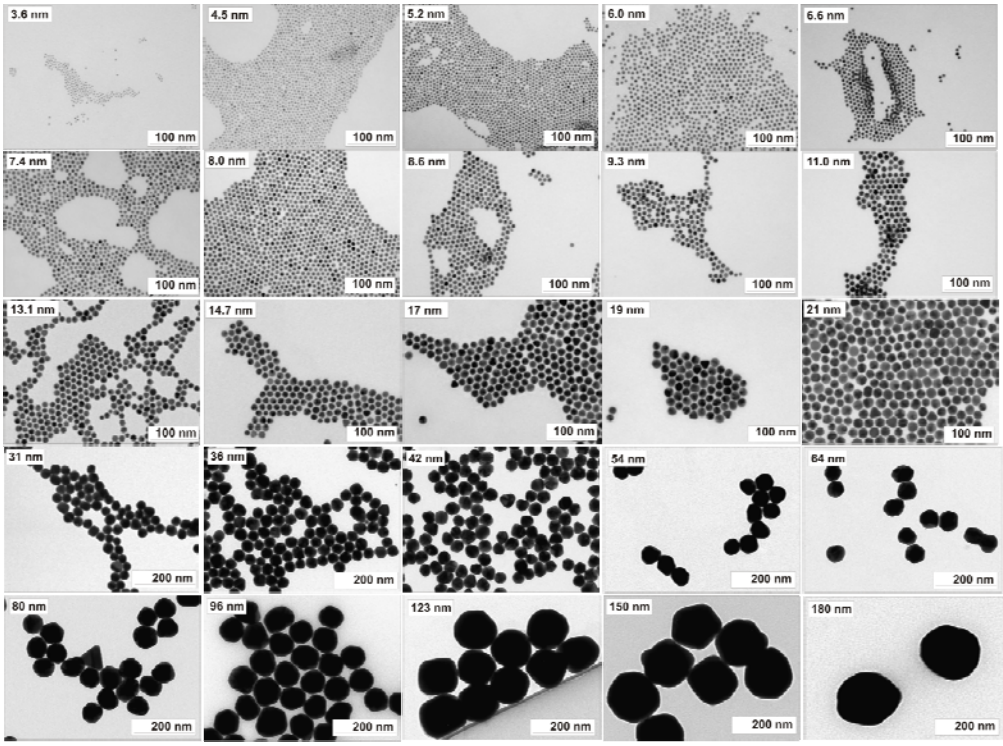
Corresponding author email: dmartrou@cemes.fr

Size-Controlled Synthesis of Citrate-Stabilized Gold Nanoparticles: Surface Reactivity, Optical and Catalytic Properties.

Neus G. Bastús[1], Jordi Piella [1], Víctor Puntes[1,2,3]

[1] Institut Català de Nanociència y Nanotecnologia (ICN2), 08193 Bellaterra, Spain.
[2] Vall d'Hebron Institut de Recerca (VHIR), 08035, Barcelona, Spain.
[3] Institució Catalana de Recerca i Estudis Avançats (ICREA), 08010 Barcelona, Spain.
email: neus.bastus@icn2.cat

Gold nanoparticles (Au NPs) are still one of the most interesting nanomaterials because of their exceptional chemical stability, catalytic activity, processability, and metallic nature, which provide them unique size-dependent optical and electronic properties. In spite of its fundamental and technological importance, the challenge of synthetically controlling their size and surface chemistry has been traditionally a challenging task. Herein, we present our recent advances on the seeded-growth synthesis of citrate-stabilized Au NPs with controlled morphology and nanometric size resolution between 3.5 and 200 nm[1-2]. The use of similar conditions and reagents for the production of all sizes allow us to properly asses the role of NP size and surface coating on their final optical and catalytic properties[3-4]. Besides, we also explore how NP size affects surface reactivity, melting effects and interactions with proteins[5]. These studies are relevant in the design of the final selectivity, activity and compatibility of Au NPs, especially in those applications where size is a critical parameter.



1. Piella, J.; Bastús, N. G.; Puntes, V., Size-Controlled Synthesis of Sub-10-nanometer Citrate-Stabilized Gold Nanoparticles and Related Optical Properties. *Chem. Mater.* **2016,** *28* (4), 1066-1075.
2. Bastús, N. G.; Comenge, J.; Puntes, V. F., Kinetically Controlled Seeded Growth Synthesis of Citrate-Stabilized Gold Nanoparticles of up to 200 nm: Size Focusing versus Ostwald Ripening. *Langmuir* **2011,** *27* (17), 11098-11105.
3. Piella, J.; Merkoci, F.; Genc, A.; Arbiol, J.; Bastus, N. G.; Puntes, V., Probing the surface reactivity of nanocrystals by the catalytic degradation of organic dyes: the effect of size, surface chemistry and composition. *J. Mater. Chem. A* **2017,** *5* (23), 11917-11929.
4. Bastus, N. G.; Piella, J.; Puntes, V., Quantifying the Sensitivity of Multipolar (Dipolar, Quadrupolar, and Octapolar) Surface Plasmon Resonances in Silver Nanoparticles: The Effect of Size, Composition, and Surface Coating. *Langmuir* **2016,** *32* (1), 290-300.
5. Piella, J.; Bastus, N. G.; Puntes, V., Size-Dependent Protein-Nanoparticle Interactions in Citrate-Stabilized Gold Nanoparticles: The Emergence of the Protein Corona. *Bioconjug Chem* **2017,** *28* (1), 88-97.

Gold Nanorods with Ultranarrow LSPR Bands

Luis M. Liz-Marzán[1,2]*
(1) *Bionanoplasmonics Laboratory, CIC biomaGUNE, Paseo de Miramón 182, 20014, Donostia – San Sebastian, Spain*
(2) *Ikerbasque, Basque Foundation for Science, Bilbao, Spain*

Although seeded-growth methods have made available to us an extensive library of anisotropic metal nanoparticles [1], the chemical complexity of the growth solution, often involving organic additives [2], and the structural instability of the seeds hinder the quest for high quality products. For the sake of synthetic simplicity, merging different synthetic protocols by finding common growth routes, is a mandatory step to reach a universal growth mechanism and reproducible fabrication. This communication will introduce two recent discoveries, related to improving the optical quality of both pentatwinned and single crystal gold nanorods.

We recently demonstrated that a thermal treatment of small seeds results in extensive twinning and a subsequent drastic yield improvement (>85%) in the formation of different types of pentatwinned nanoparticles, including nanorods, with a high monodispersity and tunable aspect ratio [3].

On the other hand, although single crystal Au nanorods can be readily obtained with very high quality directly from optimized seeded growth methods, polydispersities below 10% are still difficult to reach, which leads to some broadening of the longitudinal LSPR band. We show here that irradiation with a femtosecond laser, at selected conditions of fluence and surfactant concentration, may lead to significant narrowing of the LSPR band, even to the limit of the single particle, as calculated from theoretical models, meaning pure “optical monodispersity”.

References

1- M. Grzelczak, J. Pérez-Juste, P. Mulvaney, L.M. Liz-Marzán, Shape control in Gold Nanoparticle Synthesis. Chem. Soc. Rev. **37**, 1783 (2008).
2- A. Sánchez-Iglesias, N. Winckelmans, T. Altantzis, S. Bals, M. Grzelczak, L.M. Liz-Marzán, High Yield Seeded Growth of Monodisperse Pentatwinned Gold Nanoparticles by Seed Optimization. J. Am. Chem. Soc. **139**, 107 (2017).
3- G. González-Rubio et al., Femtosecond Laser-Controlled Reshaping of Gold Nanorods into Colloids with Ultra-Narrow Localized Surface Plasmon Resonances. Science **358**, 640 (2017).

Corresponding author email: llizmarzan@cicbiomagune.es

Twinned Gold Nanoparticles under Growth: Bipyramids Shape Controlled by Environment

Z. C. Canbek,[1] R. Cortes-Huerto,[1,3] F. Testard,[1] O. Spalla,[1] S. Moldovan,[5] O. Ersen,[5] A.Wisnet [6] G. Wang,[5] J. Goniakowski,[3] C. Noguera,[3] and N. Menguy[2]

(1) *CEA Saclay, UMR CEA/CNRS 3685 NIMBE/LIONS, Gif sur Yvette, France*

(2) *Université Pierre et Marie Curie, IMPMC, UMR 7590 CNRS, Paris, France*

(3) INSP, CNRS, UPMC, UMR7588, Paris, France

(4) IPCMS, UMR 7504, CNRS ULP, Strasbourg, France

(5) Université Paris Diderot-Paris7, LMPQ, Paris, France

(6) CeNS, Ludwig Maximilians University Munich, Germany

The control of shape and size of anisotropic gold nanoparticles (NPs) was at the center of intense research in the last 20 years in regards to their unique physical and chemical properties [1]. If control of size is nowadays achieved, questions about the mechanism promoting the anisotropy (in particular when considering the materials crystallizing in bulk in an FCC phase) are still under debate [2].

In this context, the structure of (Au) bipyramids, very promising for their specific plasmonic properties, was fully analyzed for gradual stages of growth [3]. The atomic structure of the elongated object in formation was extracted thanks to the use of HRTEM (High resolution transmission electronic microscopy) in specific conditions and SAED (selected area electronic diffraction) analysis (fig. 1). The conservation of a bulk penta-twinned structure inherited from isotropic decahedral (i-Dh) seeds all along the growth is observed for two different synthetic conditions: silver(I)-assisted or without silver seeded growth method. The key role of the initial structure of seeds in the orientation of the final shape is discussed in the framework of a recent atomistic approach [4] developed for metal-environment interactions to account for the stability of multi-twinned nanorods or bipyramids in a complex environment.

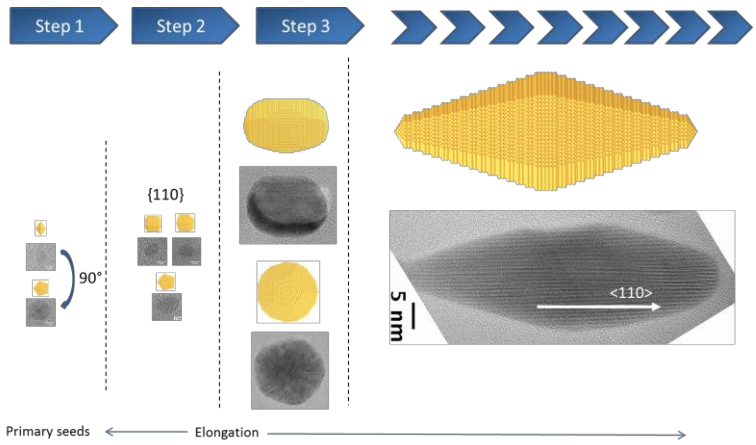


Figure 1. Schematic view of the successive steps of growing penta-twinned NPs into bipyramids.

References

1- N. D. Burrows et al, J. Phys. Chem. Lett. **7**, 632−641 (2016).
2- M. J. Walsh et al, ACS Nano **9**, 715–724 (2015).
3- Z.C. Canbek et al, Cryst. Growth Des.**15**, 3637-3644 (2015).
4- Cortes-Huerto, R.; Goniakowski, J.; Noguera, C. J. Chem. Phys.**138**, 244706 (2013).

Corresponding author email: fabienne.testard@cea.fr

Gold nanobipyramids and beyond : highly concentrated, near quantitative synthesis of pentatwinned nanostructures.

D. Chateau[1,2], S. Parola[1], S.Santucci[2]
(1) *Laboratoire de Chimie, ENS Lyon, France*
(2) *Laboratoire de Physique, ENS Lyon, France*

Among the various studied shapes of gold nanoparticles, nanobipyramids are one of the most interesting type : their anisotropic structure enables the tuning of their LSPR even further than gold nanorods, with higher local electric field enhancement, and their morphology (aspect-ratio, roughness, size, etc.) can be controlled with more freedom[1-5]. A few years ago[1], we developed in our lab a very high yield process to make such nanostructures and control their aspect-ratio, in the classic sub-millimolar concentration range. While this process was very efficient, its low concentration makes the production of concentrated solutions quite cumbersome and generates lots of waste.

Therefore, we developed a new versatile process enabling the direct preparation of gold nanobipyramids and several other pentatwinned nanostructures at concentrations between 15 and 30mM (3 to 6g per liter). This novel synthesis has nearly quantitative yields, while allowing an easy tuning of LSPR wavelength. A specific influence of the nature of the reducing agent on the morphology has been observed, and this can be further controlled or enhanced by variating experimental conditions (surfactant, temperature, co-reagents, etc.). Those breakthroughs open further uses for gold pentatwinned nanostructrures by simplifying their preparation at gram scale and tuning their morphology for specific uses with only one general process.

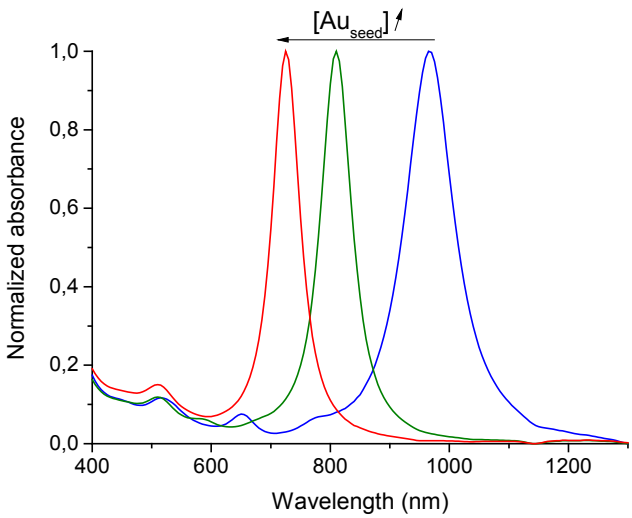


Figure 1. Spectra of various bipyramids obtained at 3 g/l at different seed concentration (diluted without any purification/centrifugation).

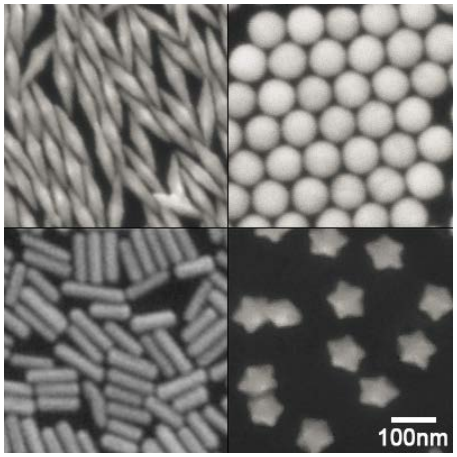


Figure 2. SEM micrographs of some gold nanoparticles prepared using our new concentrated process

References

1- D. Chateau et al., Nanoscale **7 (5)**, 1934 (2015).
2- A. Sánchez-Iglesias et al., J. Am. Chem. Soc. **139 (1)**, 107 (2016).
3- X. Kang et al., Nanoscale **9**, 5879 (2017).
4- H.-L. Wu et al., Chem. Mater. **21**, 110 (2009).
5- K. M. Mayer et al., Nanotechnology **21 (25)**, 255503 (2010).

Corresponding author email: denis.chateau@ens-lyon.fr

IMPLICATIONS ON THE GROWTH OF GOLD BIPYRAMID NANOPARTICLES FROM MOLECULAR DYNAMICS SIMULATIONS

Santosh Kumar Meena[1], Frederic Lerouge[1], Stephane Parola[1], Marialore Sulpizi[2], Ivan Rivalta[1]

(1) Université de Lyon, CNRS, École Normale Supérieure de Lyon, UMR 5182, 46 Allée d'Italie, 69364 Lyon, Cedex 07, France
(2) Department of Physics, Johannes Gutenberg University, Staudingerweg 9 55128 Mainz, Germany

Gold bipyramidal (GBP) nanoparticles show significantly higher field enhancement than nanorods, being promising candidates for sensing applications involving enhanced Raman and fluorescence spectroscopy techniques [1,2]. The plasmon resonance spectral range and the optical enhancement can be tuned through shape and size of GBP nanoparticles. However, full shape and size control during the growth is challenging since the aspect of the final nano-object depends on various factors including initial seed geometry, surfactant type and ions concentrations [3]. Here, we have investigated the role of the cetyl trimethylammonium bromide (CTAB) surfactant, as its use is crucial for GBP nanoparticle formation and stability, using atomistic molecular dynamics simulations. The surface coverage of CTAB (positively charged) heads and (bromide) counterions has been investigated on various exposed surfaces of the gold seeds, showing different behavior on side, bridge and tip facets. This difference in coverage partially explains the anisotropic growth of GBP nanoparticles, which differentiates from that of nanorods since high index facets, such as Au(113), Au(115) and Au(117), can be stabilized on the side of the nanoparticles, providing different aspect ratios of the final object[4,5]. We found that CTAB surfactant forms micellar structures also on stepped high index surfaces, with inter-micelles channels similar to those observed on nanorods [6]. However, the presence of higher CTAB coverage and narrower inter-micelles channels in GBP nanoparticles as compared to nanorods, explains the formation GBP nano-objects and their remarkable stability.

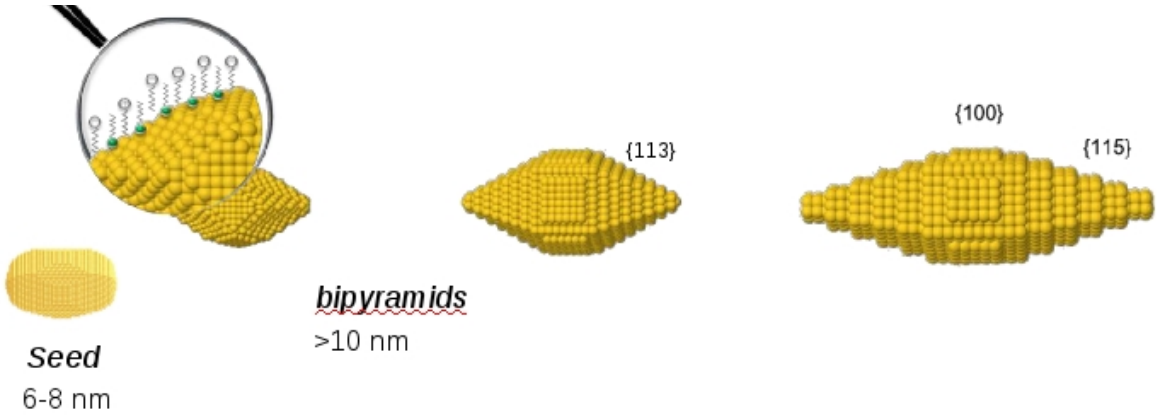


Figure 1. schematic representation of GBP nanoparticles growth

References

1- H. Zhang, Z. She, H. Su, K. Kerman, H. Kraatz, *Analyst*, **2016**, **141**, 6080–6086
2- M. Liu, P. Guyot-Sionnest, *Phys. Rev. B*, **76**, 235428 (2007).
3- Z. C.Canbek, R. Cortes-Huerto, F. Testard, O. Spalla, S. Moldovan, O. Ersen, A. Wisnet, G. Wang, J. Goniakowski, C. Noguera, N. Menguy, *Cryst. Growth Des*. **15**, 3637 (2015).
4- D. Chateau, A. Liotta, F. Vadcard, J. R. G. Navarro, F. Chaput, J. Lermé, F. Lerouge and S. Parola, *Nanoscale*, **7**, 1934 (2015)
5- J. Lee, K. Gibson, G. Chen, Y. Weizmann, *Nat. Commun.* **6**, 7571 (2015).
6- S. K. Meena and M. Sulpizi, *Angew. Chem. Int. Ed.,* **55**, 11960 (2016).

Corresponding author email: santosh-kumar.meena@ens-lyon.fr, san.iitb@gmail.com

How to synthesize gold nanocages with a precise number of windows ?

C.Hubert[1,2], A.Madeira[1], A.Desert[1], J.Majimel[1], E.Duguet[1], S.Ravaine[2], F.Vialla[3], P.Maioli[3], N.Del Fatti[3], A.Crut[3], F.Vallée[3], O.Ersen[4], I.Florea[4], M.Tréguer-Delapierre[1*]
(1) *ICMCB-CNRS, University of Bordeaux, Pessac, France*
(2) *CRPP-CNRS, University of Bordeaux, France*
(3) ILM, University of Lyon, France
(4) ICPMS, University of Strasbourg, France

Development of new objects for realizing new properties or functions is one of the major challenges in nanoscience and nanotechnology. In this presentation, we will show how gold nanocages with a precise number of windows and a well-defined morphology using sacrificial multipod-like templates can be produced. The 3D shape of the hollow nanostructures was characterized by TEM and electron tomography and their optical properties were both investigated theoretically and experimentally at the particle level. We will also describe how the synthetic method can be extended to fill the nanocages with an isotropic or anisotropic particle of different nature. This synthetic route offers the unique capability of creating new hybrid nano-objets formed by different components, and to combine and modify their individual optical properties via their components interaction.

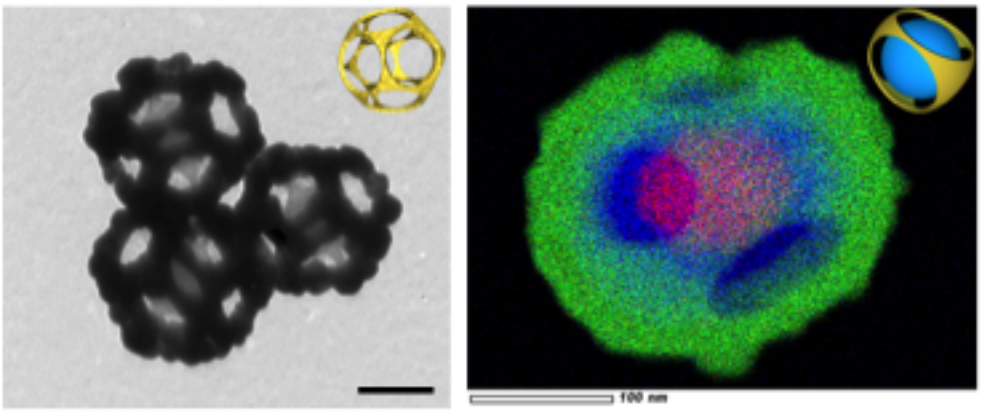


Figure 1. TEM of Au nanocages with 12 windows / Cartography of a Au nanocage with four windows filled with a magnetic particle

References
1- C.Chomette and al. , Chem.Nano.Mat, 3, 160 (2017)
2- C.Hubert and al., Colloids and surface A (2016)
3- C.Chomette and al., Faraday discussion (2016)

Corresponding author email: treguer@icmcb-bordeaux.cnrs.fr

From Au or Ag clusters to nanoparticles: an ab initio and atomistic study

C. Dulong[1], B. Madebene, J. Richardi[2]

(1) *Sorbonne Université, CNRS, MONARIS, UMR 8233, 4 place Jussieu, Paris, 75005 France.*
(2) *Sorbonne Université, CNRS, LCT, UMR 7616, 4 place Jussieu, Paris, 75005 France.*

For two decades intriguing physical/chemical properties have been reported for noble metal nanoparticles coated by ligand molecules [1]. In order to better understand the metal/ligand interactions which govern in part the morphology of these objects, numerical simulations are widely used. These are mainly based on two theoretical models: on one hand ab initio calculations (Density Functional Theory, DFT) and on the other hand atomistic simulations. If DFT allows an accurate description of the systems (electronic level) its use is unfortunately limited either to very small clusters or to periodic surfaces due to computational cost. Atomistic models allow a simulation of a whole coated nanoparticle [2] (from 5 nm to 9 nm) at the expense of electronic structure information. Futhermore classical force fields are unable to describe bond formation/breaking and so structural deformation/reorganization, the "staple" motif [3], as well as atomic diffusion on the surface of nanoparticles. However Reactive Force Fields (ReaxFF) have been developed to reproduce bond breaking [4] which could be an effective tool to compare Gold or Silver nanoparticle/ligand interaction.

In this presentation we will first introduce limits of Gold-Gold and Gold-thiolate ReaxFF results compared to ab initio data. Consequently both Gold-Gold and Gold-ligand ReaxFF need to be improved and Silver-Silver Silver-ligand ReaxFF have to be developed. We chose a set of Gold or Silver model systems as pyramidal clusters or both (111) and (100) surfaces in interaction with ligand molecules in order to determine preferential sites of reaction and structural deformations (DFT calculations). In a same time a topological analysis using the Quantum Theory of Atoms In Molecules (QTAIM) and Electron Localization Function (ELF) methods allows us to characterize the metal-metal and metal-ligand chemical bond nature and differences of reactivity between Gold and Silver nanoparticles through the behavior of electronic densities. We will present these ab initio results following by their topological analysis for atomic sulfur, alkane thiolate and alkane thiol as ligands.

References

1- M. C. Daniel, D. Astruc, Chem. Rev. 101,2991-3024 (2001)
2- T. Djebaili, *Thesis,* UPMC (2014)
3- H. Häkkinen, Nature Chem., 4, 443-455 (2012)
4- A. C. T. Van Duin, *et al.,* J. Phys. Chem. A, 105,9396-9409 (2001)

Corresponding author email: clement.dulong@upmc.fr

Au···H hydrogen bonds in ligand-coordinated gold clusters

Katsuaki Konishi,[1,2] M. Abu Bakar,[2] Yukatsu Shichibu.[1,2]
1 *Graduate School of Environmental Science, Hokkaido University, Sapporo, 060-0810, Japan*
2 *Faculty of Environmental Earth Science, Hokkaido University, Sapporo, 060-0810, Japan*

For several decades, M···H interatomic forces, such as agostic and hydrogen-bonding interactions, have attracted continuing interest not only from the fundamental aspects but also in relation to their involvement in some catalysts. For gold, plenty of examples of close contacts with hydrogen atoms have been reported in the crystal structures of Au^{-}, Au^{+} and Au^{3+} complexes, but there has been limited decisive experimental evidence of such attractive interactions [1]. Especially, no examples of spectroscopically identified "hydrogen-bond-type" Au···H interactions have been reported. This is contrasted with the cases of the other transition metal complexes, which provide numerous examples of M···H hydrogen bonds.

Herein we demonstrate the first example of spectroscopically identified hydrogen bonding interaction of C-H units to Au atoms in divalent hexagold cluster ($[Au_6]^{2+}$) decorated by diphosphine ligands [2]. Ligand-protected gold clusters have currently attracted attention as a class of molecule-like metal species residing between particles and simple complexes. We have recently reported some subnanometer-sized diphosphine-coordinated clusters and revealed their unique structures and optical properties [3]. The cluster we used here is core+exo type Au6 cluster carrying *m*-phenylene-bridged diphosphines (**1**), whose crystal structure showed close contacts of the gold framework to the bridging *m*-phenylene units (Fig. 1). The hydrogen atoms at the 2-position of the *m*-phenylene bridges (H-2) are located in proximity to the tetrahedral core with Au-H distances of 2.60 – 2.65 Å, which are fairly shorter than the sum of the van der Waals radii (2.86 Å). Accordingly, the distances to the nearest neighbour C atoms (3.641 – 3.699 Å) were explicitly shorter than when C, H and Au atoms are aligned with van der Waals Au-H contact (3.95 Å). The Au-H-C angles for the above short Au-H contacts were in the range of 162.0 - 171.0°. These observations imply the presence of hydrogen-bond-type interactions between the H-2 atoms and the Au cluster unit. It should be noted that the Au···H-C interactions were also observed in solution NMR, which showed ^{1}H and ^{13}C NMR signals of the C-H units at considerably downfield regions, indicating the hydrogen-bond character of the interactions. We also show the presence of electronic coupling between the Au6 moiety and bridged benzene rings in the absorption spectra. These results demonstrating the unique capability of small gold cluster to interact with unfunctionalized C-H groups may not only promote the further understanding of chemical bonding but also shed light on the elucidation / developments of recently emerging gold cluster catalysis, which would expand the scope of gold clusters.

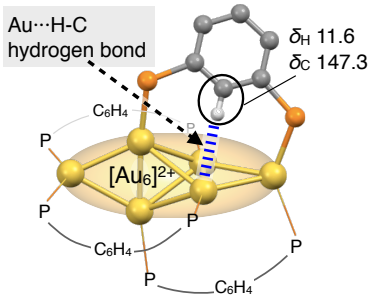


Fig. 1. Schematic illlustration of the structure of **1**.

References

1- H. Schmidbaur et al., Chem. Soc. Rev. **43**, 345 (2014).
2- Md. A. Bakar, M. Sugiuchi, M. Iwasaki, Y. Shichibu, K. Konishi, Nature Commun. **8**, 576 (2017).
3- K. Konishi, M. Iwasaki, M. Sugiuchi, Y. Shichibu, J. Phys. Chem. Lett. (*Perspectives*) **7**, 4267 (2016); K. Konishi, Struct. Bonding, **161**, 49 (2014).

Corresponding author email: konishi@ees.hokudai.ac.jp

One-pot Synthesis and Structure of $Au_{23-x}Ag_x(SR)_{15}$ Nanocluster

Chao Liu[1*], Jiahui Huang[1]
(1) Dalian Institute of Chemical Physics, CAS, Dalian, China.

The structure of nanoparticles plays a critical role in dictating their material properties. Here, we report crystal structure and optical properties of a new Au-alloy nanocluster, $[Au_{23-x}Ag_x(SR)_{15}]$ (where R = $C_{10}H_{15}$). The crystal structure and composition were determined unambiguously by single-crystal X-ray crystallography. The optical and electronic structure of clusters was studied experimentally and by DFT calculation. The crystal of $[Au_{23-x}Ag_x(S\text{-}Adm)_{15}]$ nanocluster adopts monoclinic space group $P2_1/n$. Structural dissection reveals that $[Au_{23-x}Ag_x(SR)_{15}]$ comprises an $Au_{13-x}Ag_x$ icosahedra core, three $Au_3(SR)_4$ and AgS_3 staple motifs. It is very interesting that AgS_3 as a motif exist in AuAg alloy. The Uv-vis absorption spectrum of $[Au_{23-x}Ag_x(S\text{-}Adm)_{15}]$ nanocluster shows distinct peaks at 780 nm, 600 nm, 550 nm, 440 nm and 400 nm. The experimentally observed peak at 780 nm is due to a HOMO–LUMO transition. In other word, peak at 780 nm is from transition of Au (sp) to Au (sp), and by extrapolating the optical absorbance to zero the HOMO–LUMO gap is determined to be approximately 1.5 eV, much smaller than the gap of the $[Au_{23}(SR)_{16}]$[1-2]. The unique structure of the gold/silver nanocluster may be promising in catalytic applications.

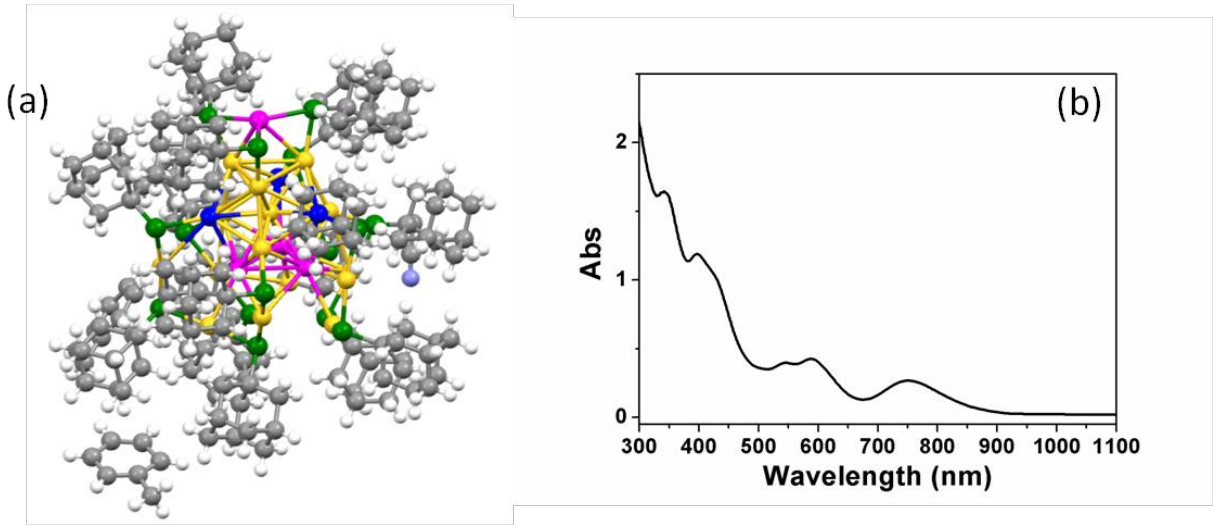


Figure 1. (a) X-ray structure of $[Au_{23-x}Ag_x(S\text{-}Adm)_{15}]$. Yellow: gold, purple: silver, blue: Au/Ag, green: sulfur, grey: carbon, white: hydrogen. (b) experimental optical absorption spectra of $[Au_{23-x}Ag_x(S\text{-}Adm)_{15}]$ nanocluster.

References

1- D, A; L, T; N, K ; Z, CJ; R, NL; J, RC; 135, 18264 (2017)
2- Li, Q.; L, T. Y.; T, M. G.; W, S.; Z, X.; S, Y.; M, G.; R, N. L.; Jin, R., Science Advances, **3**, DOI: 10.1126/sciadv.1603193 (2017).

Corresponding author email: chaoliu@dicp.ac.cn

A Series of Intrinsically Chiral Gold Nanocage Structures

X.J. Liu[1], I.P. Hamilton[1*]

(1) *Department of Chemistry and Biochemistry, Wilfrid Laurier University, Waterloo, Canada N2L 3C5*

We present a series of intrinsically chiral gold nanocage structures, Au_{9n+6}, which are stable for n ≥ 2.[1] These structures consist of an Au_{9n} tube which is capped with Au_3 units at each end. Removing the Au_3 caps, we obtain a series of intrinsically chiral gold nanotube structures, Au_{9n}, which are stable for n ≥ 4. The intrinsic chirality of these structures results from the helicity of the gold strands which form the tube and not because an individual Au atom is a chiral center. The symmetry of these structures is C_3 and substructures of gold hexagons with a gold atom in the middle are particularly prominent. We focus on the properties of Au_{42} (C_3) and Au_{105} (C_3) which are the two smallest gold nanocage structures to be completely tiled by these Au_7 "golden-eye" substructures. Our main focus is on Au_{42} (C_3) since gold clusters in the 40–50 atom regime are currently being investigated in gas phase experiments. We show that the intrinsically chiral Au_{42} cage structure is energetically comparable with previously reported achiral cage and compact Au_{42} structures. Cage structures are of particular interest because species can be encapsulated (and stabilized) inside the cage and we provide strong evidence that Au_6@Au_{42} (C_3) is the global minimum Au_{48} structure (see Figure 1). The intrinsically chiral gold nanocage structures, which exhibit a range of size related properties, have potential applications in chiral catalysis and as components in nanostructured devices.

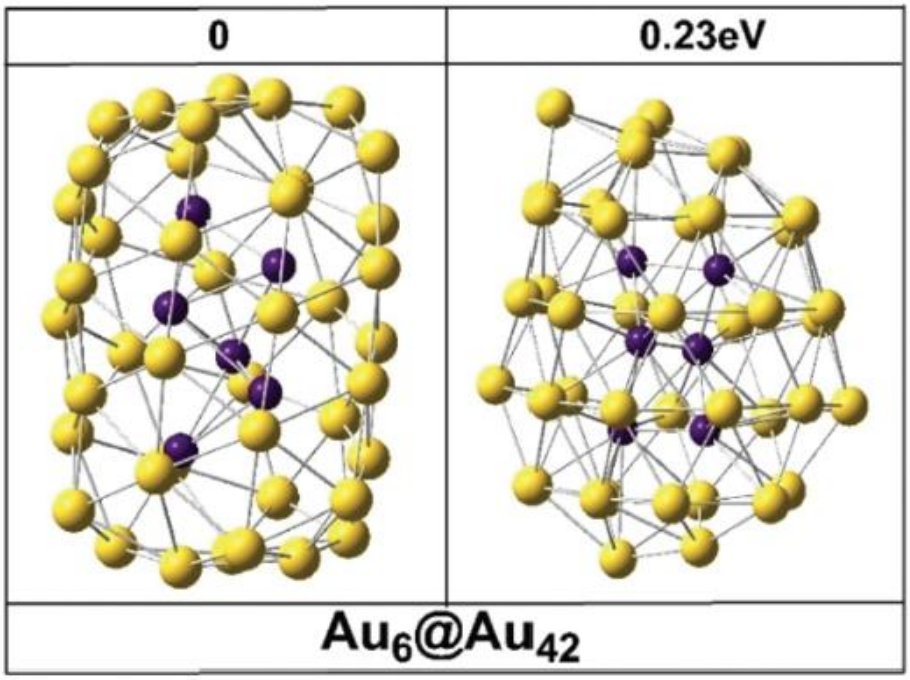


Figure 1. Au_6@Au_{42} (C_3) (left panel) and Au_6@Au_{42} (C_1) (right panel).

References

1- X.J. Liu and I.P. Hamilton, Nanoscale **9**, 10321 (2017).

Corresponding author email: ihamilton@wlu.ca

The active centers of oxygen adsorption on thiolate-protected gold clusters in various solvents

N. Nikitina, D. Pichugina, N. Kuz'menko
M.V. Lomonosov Moscow State University, Moscow, Russia

Thiolate-protected gold clusters have attracted considerable interest due to their unique structure and properties. They have been used widely in many fields: catalysis, biomedicine, electronics and other fields. Precisely defined atomic composition is characteristic for thiolate-protected gold clusters, this allows to establish the relationship between structure and properties. It should be mentioned that the mechanism of molecular oxygen interaction with clusters has been unclear yet and how this affects different processes: formation, reconstruction, catalytic processes.
The aim of the work is to simulate the interaction of O_2 with $Au_{20}(SCH_3)_{16}$ and its fragments and compare this process in gas phase, water and toluene. The DFT/PBE and SBKJC basis set were used in PRIRODA and Gaussian programs.
The interaction of oxygen with the gold atom is very weak in $Au_{20}(SCH_3)_{16}$_O_2 complexes without pre-activation. Two methods of pre-activation were considered: the photophysical activation way with using singlet oxygen and the removing ligand of the gold cluster. The reactions of singlet oxygen and $Au_{20}(SCH_3)_{16}$, and its fragments ($CH_3S(AuSCH_3)$, $CH_3S(AuSCH_3)_3$, $(AuSCH_3)_8$) cluster are favorable. The O_2 adsorption energies on apart staple motifs are higher than on the cluster. This indicates that the separate fragments can really participate in oxygen activation. The molecular oxygen adsorption energies on different staple motifs are reduced by 11-12 kcal/mole, when modeling this process in water or toluene. This indicates that the homogeneous oxidation reaction is less favorable than the heterogeneous one.
The high dissociation barriers indicate that the oxygen on the cluster remains in molecular form. The electron-donor groups with respect to sulfur (some groups containing nitrogen) in the ligand increase the energies of $^1O_2$ interaction with the cluster in contrast to the electron-acceptor ones (a phenyl ring or carboxyl, hydroxyl groups).
At the thermal activation only with the certain amount of removed thiolate ligands, the oxygen adsorption becomes favorable. The de-thiolation with three ligands from various staple motifs makes possible the molecular oxygen adsorption. According to results, the $^3O_2$ adsorption energies at the thermal activation decreases in the order $CH_3S(AuSCH_3)_3^-$ > $(AuSCH3)_8$ > $CH_3S(AuSCH_3)_2^-$. This confirms that a negative charge doesn't play a significant role in the oxygen adsorption.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 17-03-00962.

References:
[1] C. Zeng, C. Liu, Y. Chen, N.L. Rosi, R. Jin., J. Am. Chem. Soc. **136**, 11922 (2014).

Corresponding author email: nnikitina1719@gmail.com