Supercrystals of noble metal nanoparticles: lattice packing and plasmonic properties

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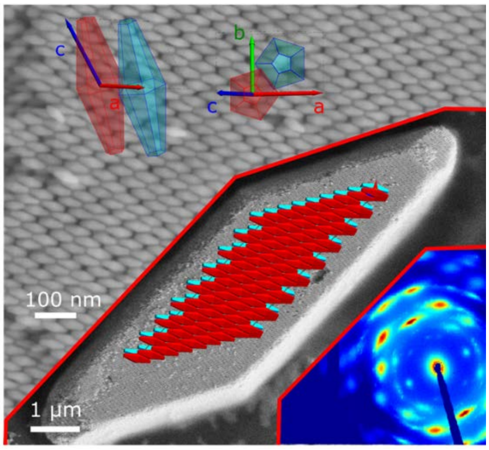

Background At least since Ancient Greece, natural scientists have been fascinated by the way identical bodies pack together in regular assemblies. The vast majority of their efforts has concerned isometric objects (with a similar size along the three space directions), such as spheres and Platonic or Archimedean solids (full or truncated regular polyhedra, respectively), both experimentally and theoretically or numerically. However, much less work has been done on elongated particles, such as ellipsoids or spindles.
More recently, noble metal nanoparticles (NPs) have generated sustained interest because of their striking optical properties, due to collective oscillation of the conduction electrons. This phenomenon is known as localized surface plasmon resonance (LSPR) and leads to intense colors in the far field and strong electromagnetic fields at the surface of the particles, with applications in many research areas, such as biosensors, imaging, therapy, nanophotonics, catalysis and light harvesting.
In this context, the assembly of NPs in large scale lattices or supercrystals (SCs) has both fundamental and practical significance. On the one hand, their excellent shape regularity and large density make them ideal candidates for achieving compact and ordered packings; on the other hand, the LSPRs are exquisitely sensitive to the interparticle distance and orientation, so that small changes in the SC structure can lead to large variations in their optical properties.
Goals and strategy During this project, we will:

1. Assemble **anisotropic** metallic nanoparticles into three-dimensional SCs.
2. Elucidate the inner structure of the assemblies by small-angle X-ray scattering (SAXS), in combination with traditional scanning electron microscopy (SEM) and with an elaborate version that combines it with a focused ion beam (FIB) [1].
3. Test theoretical results and conjectures on the packing of ellipsoids [2].
4. Follow by absorbance spectroscopy (AS) the LSPRs of the SCs and understand their dependence on the SC structure.

We will use a multidisciplinary approach, combining sample preparation (NP synthesis and assembly) with several state-of-the-art techniques (direct imaging, scattering and spectroscopy) and with in-depth analysis of the resulting data. The expected results will complete an ongoing research project that has already been very fruitful in elucidating the structure of complex packings [3,4].

The chemical synthesis work will be done in close collaboration with Cyrille Hamon (CNRS researcher) and Claire Goldmann (CNRS engineer) at the Laboratoire de Physique des Solides (LPS) in Orsay. The SAXS measurements will be performed at the ICS, but also at the SOLEIL synchrotron (on the SWING beamline), where beamtime is already available. SEM will mainly be performed on the microscopy platform of the ICS, but the FIB-SEM tomograms will be done in the group of Andrey Chuvilin in San Sebastian, Spain.

[1] D. García-Lojo, E. Modin, S. Gómez-Graña, M. Impéror-Clerc, A. Chuvilin, I. Pastoriza-Santos, J. Pérez-Juste, D. Constantin, and C. Hamon, *Structure and Formation Kinetics of Millimeter-Size Single Domain Supercrystals*, Adv. Funct. Mater. **31**, 2101869 (2021).
[2] A. Donev, F. H. Stillinger, P. M. Chaikin, and S. Torquato, *Unusually Dense Crystal Packings of Ellipsoids*, Phys. Rev. Lett. **92**, 255506 (2004).
[3] J. Lyu, W. Chaâbani, E. Modin, A. Chuvilin, T. Bizien, F. Smallenburg, M. Impéror-Clerc, D. Constantin, and C. Hamon, *Double-Lattice Packing of Pentagonal Gold Bipyramids in Supercrystals with Triclinic Symmetry*, Adv. Mater. **34**, 2200883 (2022).
[4] J. Marcone, W. Chaâbani, C. Goldmann, M. Impéror-Clerc, D. Constantin, and C. Hamon, *Polymorphous Packing of Pentagonal Nanoprisms*, Nano Lett. **23**, 1337 (2023).