

# How do plasmonic polymers assemble? A structural study

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**Background** The enduring fascination with noble metal (Au, Ag) nanoparticles (NPs) is explained by their striking optical properties, due to collective oscillation of the conduction electrons. This phenomenon is known as localized surface plasmon resonance 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.

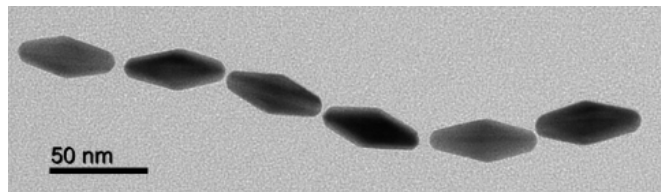


Figure 1: Chain of self-assembled gold bipyramids [4].

Moreover, these plasmonic properties can be tuned by directed self-assembly: the NPs are brought close together (see Figure 1), dramatically increasing the electromagnetic fields at interparticle gaps, in regions known as *hot spots*. Many assembly strategies are being used, and the final structures are studied by transmission electron microscopy (TEM) while the kinetics is followed via UV-Vis-IR absorbance spectroscopy (AS). However, this technique does not provide structural information.

**Goals and strategy** We will follow the assembly process of gold NPs of various shapes (spheres, rods, bipyramids, tetrapodes) by scattering techniques and AS. In a recent publication [1], we have shown that the sulfate-induced assembly of gold NPs takes place in two steps (see Figure 2) and that the combination of small-angle X-ray scattering (SAXS) and AS is crucial for a full understanding of the process. We will extend this strategy by using dynamic light scattering (DLS), which gives access to the size of the aggregates.

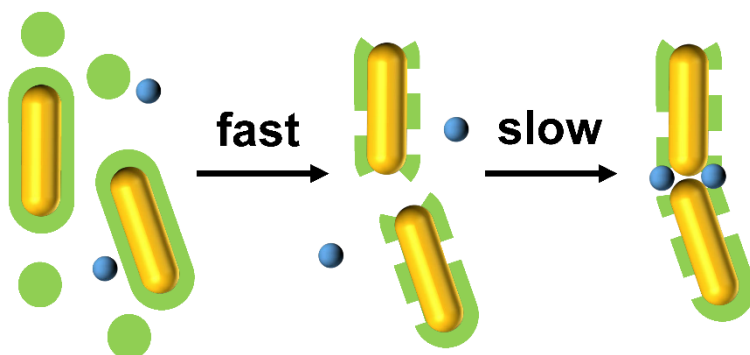


Figure 2: Sulfate-induced assembly of gold nanorods takes place in two steps: fast aggregation induced by lowering the surfactant concentration and slow structuring of these aggregates, mediated by sulfate ions. Only the second step is detectable via AS spectroscopy [1].

The combination of three time-resolved techniques will yield unprecedented insight into the kinetics: the yield, reaction order, rate constant and ultimately the nature of the process (chain or step-growth polymerization, etc.) will become available.

The assembly will be induced by the addition of dithiol linkers with different lengths in order to control the interparticle distance [2], or by grafting the particles with polystyrene chains and changing the quality of the solvent (via addition of water to THF) [3]. The 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.

Finally, we will study the resulting assemblies by advanced microscopy techniques, available in the microscopy group of the LPS, in order to determine the plasmonic properties of individual objects [4] and improve their suitability for applications, such as the detection of minute amounts of analytes by surface-enhanced Raman scattering.

- [1] Lyu, J., et al. Two-step assembly kinetics of gold nanoparticles. *J. Mater. Chem. C*, in press (2021).
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- [3] Sánchez-Iglesias, A. et al. Hydrophobic Interactions Modulate Self-Assembly of Nanoparticles. *ACS Nano* **6**, 11059 (2012).
- [4] Li, X. et al. Plasmonic Oligomers with Tunable Conductive Nanojunctions. *J. Phys. Chem. Lett.* **10**, 7093 (2019).