Metal colloids investigated by enhanced-Raman correlation spectroscopy

Metal colloids are suspensions of nanometre-size gold or silver particles dispersed in a liquid, here water. Under illumination by light, these solutions present unique and amazing optical properties that depend strongly on the size, shape and state of aggregation of the particles. However in spite of intense research work dedicated to metal colloids, understanding their optical properties in relation with the geometry of the particles as well as investigating their aggregation processes still poses a highly challenging task. Combining correlation analysis with Raman scattering measurements answers this challenge.

The rich optical properties of metal colloids are governed by the localized surface-plasmon modes of their constituent nanoparticles. These resonances are collective oscillations of the free electrons at the surface of the metal. They can be excited by light, which gives rise to resonantly-enhanced light absorption and emission properties as well as enhancement of the electric and magnetic fields at the nanoparticle surface.

Depending on various physical or chemical parameters (temperature, pH, adsorbed molecules...) nanoparticles may aggregate to form clusters ranging from simple dimers up to large and (more or less dense) fractal clusters composed of hundreds of particles. The electromagnetic interactions between the nanoparticles induce additional and stronger plasmon resonances than those of the individual particle, leading to possibly-total absorption of the incident light or to giant enhancements of the electromagnetic field in the nanoscale regions in between the particles.

These enhanced fields are in great part responsible for the so-called Surface-Enhanced Raman Scattering (SERS) effect, the enhancement by several orders of magnitude of the Raman scattering (*i.e.* the inelastic scattering of light) by molecules when they are adsorbed on the nanoparticles and trapped in such high field regions. As a consequence, metal colloids are currently used for ultra-sensitive detection of molecules, with wide applications in physics, chemistry, and biology. They are also very promising prospective candidates for in-vivo medical applications, such as intracellular imaging or in-body drug delivery, and are under investigation in the field of nanoscale thermally-activated processes such as nanocatalysis or photothermal therapy.

If the case of dimers is well understood, adding more nanoparticles rapidly increases the complexity of the system, hence posing a non-trivial task to relate their measured optical properties to those of an individual nanoparticle. There is consequently a need for in-situ characterizations of the aggregates and the aggregation processes, including the very first steps of the aggregation process.

To achieve this, we have developed an original experimental technique that associates correlation analysis with SERS spectroscopy (Fig. 1). A laser beam is tightly focused in the colloidal solution via a confocal microscope thus providing a very small observation volume. The laser beam excites the nanoparticles' plasmon-resonances responsible for enhancing the Raman scattering associated with excitations of the vibrations of the molecules adsorbed on these particles. We record the fluctuations of the Raman intensities as the particles diffuse in and out of the small observation volume, and we analyse these temporal fluctuations via auto-correlation functions (the correlations of the Raman signal with itself, at points separate in time), see Fig. 1. The correlation functions provide a characteristic time-value from which the nanoparticles' diffusion coefficient is inferred. Rotation of anisotropic clusters within the focus volume also provokes temporal fluctuations of the intensities, giving rise to a second characteristic time related to the rotational diffusion coefficient of the nanoparticles and/or clusters. From the values of the diffusion and rotation coefficients, and using hydrodynamic models, the size and shape of the nanoparticles/clusters can be identified.

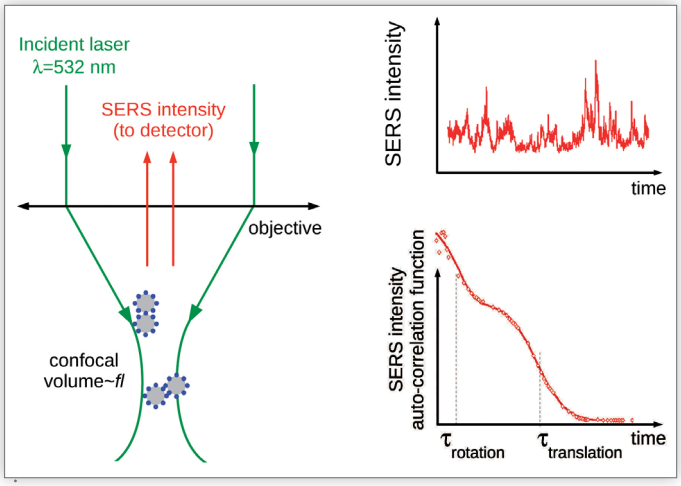

Fig. 1: At left: *A microscope illuminates a colloidal solution of nanoparticles (grey circles) carrying adsorbed molecules (blue dots). The Surface Enhanced Raman Scattering by the molecules, in the backwards direction, is recorded as a function of time* ***(top right)****. The auto-correlation function* ***(bottom right)*** *yields rotational and translational characteristic times related to the geometry of the diffusing objects.*

As a proof-of-principle we studied a model system of aggregates of ~30 nm diameter silver nanoparticles where the coagulation of the nanoparticles was induced by p-mercaptobenzoic acid (MBA) molecules. Depending on the MBA concentration, ranging from 1 to 10^{-3} millimoles/litre, different aggregation stages could be achieved and identified. For the highest concentration in MBA, we showed that large, isotropic clusters with an effective hydrodynamic radius almost 30 times larger than that of the isolated nanoparticle were formed. At lower MBA concentrations the first stages of the aggregation process could be studied. Dimers and chains of four nanoparticles were observed. Finally, in the case of the lowest MBA concentration, no aggregation occurred and the diffusion of the isolated nanoparticles of the initial colloidal solution was observed.

These results show that Surface-Enhanced Raman Scattering correlation spectroscopy is a very promising and powerful technique for in-situ studies of this kind. It enables the quantitative sizing and characterization of SERS-active aggregates and isolated nanoparticles. It thus paves the way to the practical task of in-situ monitoring of nanoparticle aggregation processes, in conjunction with basic research into the optical properties of the as-formed clusters.

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FURTHER READING

"SERS correlation spectroscopy of silver aggregates in colloidal suspension: quantitative sizing down to a single nanoparticle"
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