Signature of the anisotropy of two-photon excited luminescence of nearly spherical gold particles diffusing in solution.

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Here, we report on the properties of the two-photon excited luminescence of gold nanobeads dispersed in solution.

Nanometallic objects derive their optical properties from an ability to support collective electronic excitations, known as surface plasmons. In the case of gold, a further interest of the particles is their biocompatibility and their ability to be suitable platforms for biophotonics. A lot of studies have been recently devoted to functionalise gold particles to create sensitive hybrid probes for molecular recognition and biosensing. The corresponding approach generally takes advantage of the modulation of the fluorescence properties of a chromophore in close vicinity to the gold core. The emission properties, enhancement or quenching, depend on the photophysical properties of the linked molecules, on the plasmon resonances of the core and on their interaction [1, 2]. The potential of such hybrid probes relies on the tuning the plasmon resonances by shaping the gold core.

Apart from fluorescent functionalisation with linked chromophores, a growing field of research is dedicated to targeted imaging with gold particles as contrast agents because of reduced photoxicity and versatility of excitation, in particular. The optical process involved in imaging is the emission of luminescence, following either one or two photons absorption. Excitation in the near-infrared domain is the rule under two-photon excitation [3] but it can be used even with one photon excitation in the case of nanorods for example. It combines the advantages of being less toxic for the samples and of deeper penetration into the tissues. Another interesting application is the thermal effect related to absorption when the excitation wavelength is close to their plasmon resonance peaks. The latter has been demonstrated to be of interest for therapeutic purposes [4].

The initial aim of our studies was to determine if the two-photon excited luminescence process could be efficient enough to track small spherical gold nanobeads diffusing in aqueous solutions. It implied to work at the single particle level. In fact, luminescence of gold nanoparticles has been mainly studied on deposited samples, eventually at the single particle level but very few experiments have been performed on liquid samples, generally with a rather high concentration of particles.

To understand the optical behavior of gold nanobeads, we have used Fluorescence Correlation Spectroscopy (FCS) implemented on a two-photon microscope comprising imaging capabilities. As is displayed on the Figure 1, the cross-correlation profile of the two-photon excited luminescence of golds beads of 20 nm diameter presents an unexpected component in the microsecond temporal range. This contribution has been attributed to the signature of the Brownian rotation of the beads, using an original dual method correlating luminescence and Rayleigh scattering signals [5]. We will report on a multiparameter analysis of the two-photon excited luminescence of gold nanobeads, which reveals the

role played by the ligands capping the particles in the anisotropy of the emission. The latter is closely related to the temperature increase at the water-ligands interface following absorption. The effects of the polarization and of the excitation wavelength will be discussed.

References

[1] Dulkeith E., Morteani A. C., Niedereichholz T., Klar T. A., Feldmann J., Levi S. A., Van Veggel F. C. J. M., Reinhoudt D. N., Möller M. and Gittins D. I., Phys. Rev. Lett., **89 (**2002) 203002.

[2] Loumaigne M., Praho R., Nutarelli D., Werts M. H. V. and Débarre A., PCCP, **12** (2010) 11004.

[3] Wang H., Huff T. B., Zweifel D. A., He W., Low P. S., Wei A. and Cheng J.-X., PNAS, **102** (2005) 15752.

[4] Huang X., El-Sayed I. H., Qian W. and El-Sayed M. A., JACS, **128** (2006) 2115.

[5] Loumaigne M., Richard A., Laverdant J., Nutarelli D. and Débarre A., Nano Lett., **10** (2010) 2817.

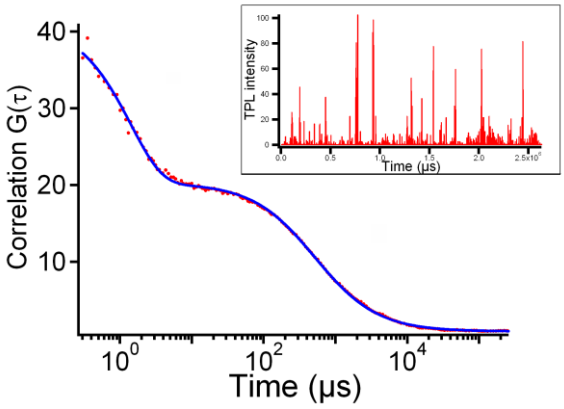

Figure 1. Cross-correlation profile of two-photon excited luminescence of gold beads of 20 nm diameter; excitation wavelength 815nm; power 6mW; In inset, histogram of bursts.