ESRF	**Experiment title:** Nanobubbles from photo-excited metallic nanorods	**Experiment number**: SI 2242
Beamline: ID09B	**Date of experiment**: from: 02-05-2013 06-05-2013	**Date of report**: 09-09-16
Shifts: 15	**Local contact(s)**: M. Wulff, G. Newby	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. A. Plech*

Dr. S. Ibrahimkutty*

Report:

The background of this experiment is the understanding of dynamics and energetics of metal nanoparticle excitation by pulsed lasers. Their resonances in the visible spectral region makes them very useful as nanoscale targets to non-contact light induced manipulation of materials and biological tissue. Together with antigen-antibody recognition such procedures gain interest in biological applications. Earlier we have clarified mechanisms in spherical gold particles excited by femtosecond pulses that lead to particle heating and cooling [1], explosive water boiling and nanobubble formation [2-4], particle ablation [5] or impact on adsorbed proteins [6]. In total most of these processes are understood by photothermal conversion and subsequent heat transfer. Except for time scales and fluence scales shifting monotonously with different particle sizes, a generic “phase diagram” for the observed reactions as function of fluence and delay after laser excitation could be established [7]. The tools are firstly X-ray wide angle scattering, which delivers information about nanoparticle lattice heating and possible melting, as well the change of state of the surrounding water (compression). Secondly small-angle scattering characterised mesoscopic shape changes, such as particle deformation, destruction or formation of nanoscale vapour bubbles around the particles. Requirement for a resolution of the dynamics are a large quantity of nanoparticles, a good size distribution and a careful setup of the laser excitation for a homogeneous fluence setting.

From an application point of view non-spherical particles offer advantages, such as the tuning of the resonance (plasmon) at will with the particle shape. In particular gold nanorods have received much attention in the past, because there are chemical synthesis methods available for a size-defined production as well as the possibility to shift the plasmon over hundreds of nanometers in wavelength. In particular a recent protocol [8] has eased this endeavour strongly. X. Ye, et al., *Nano Lett.* 13 (2013) 765.

We have excited nanorod suspension with defined plasmon position by femtosecond laser pulses at 800 nm in order to resolve the dynamics and in particular test it against recent proposals of how low-threshold bubble formation could occur by resonance excitation [9,10].

The data is quite comprehensive and a similar phase diagram to that of spheres can be proposed, however, with higher complexity. First, rods aligned with laser polarization have different thresholds

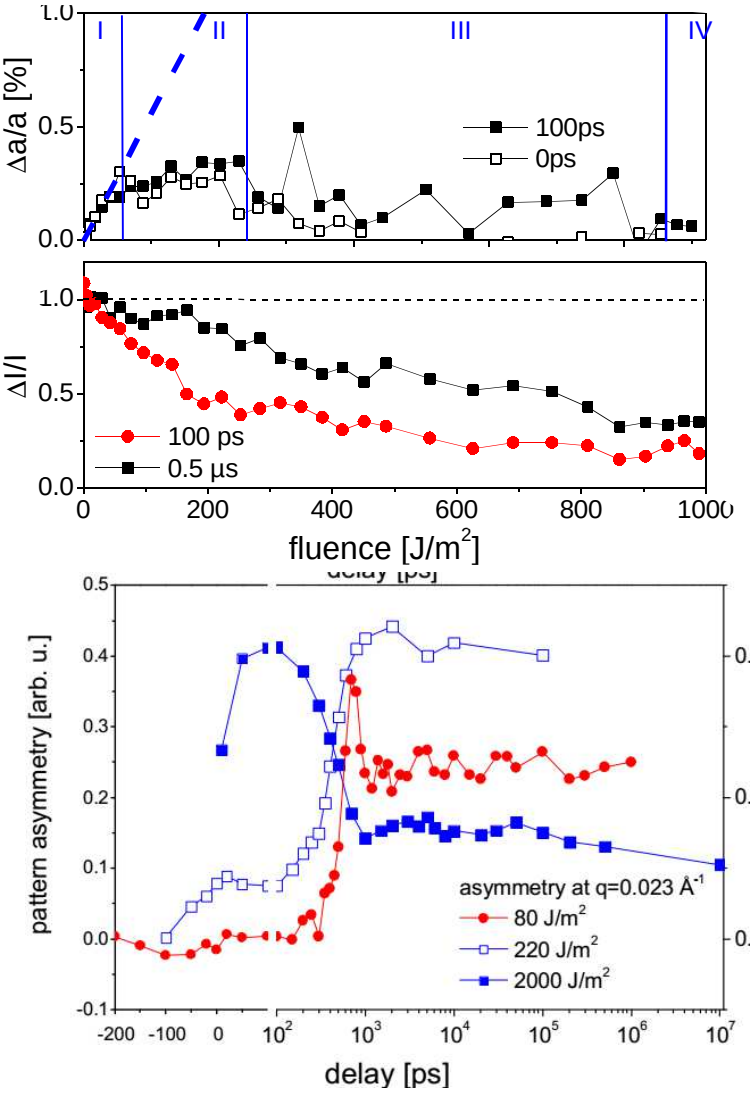
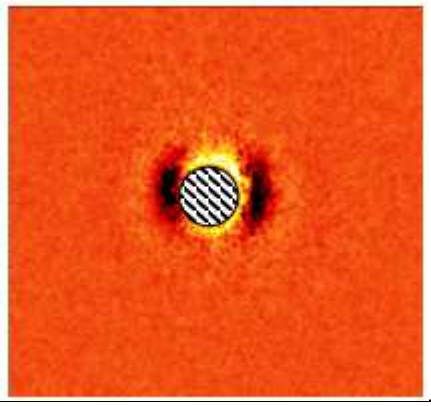


Fig. 1*: Change of the gold (111) powder peak as function of fluence for different delays. The peak shift displays the gradual heating, whereass the intensity reflects melting and irreversible changes. The regions can be characterized by: I reversible heating linearly with fluence, II irreversible excitation of part of the nanorods (those parallel to laser polarisation) and at III also other oreitnations start to be affected. In region 4 the complete powder scattering is lost.*

Fig. 2: *Anisotropy of the SAXS pattern as function of delay and laser fluence, a typical difference SAXS pattern is shown below, the excited rods are supposed to stand vertical*



from those in other directions (antenna effect). One second effect should be briefly pointed out, as seen in fig. 2. At the lowest fluence of 80 J/m^2 modification starts at some tens of picoseconds in agreement with the time resolution of the experiment and ends in a constant anisotropy level. The small spike around 500-700 ps is a transient from a nascent vapour bubble. Thus both thresholds are very close to each other. Further data has been analysed and is now put in context for publication.

[1] A. Plech, et al.: *Laser-Induced heating and melting of gold nanoparticles studied by time-resolved x-ray scattering*, Phys. Rev. B 70 (2004) 195423.

[2] V. Kotaidis, C. Dahmen, G. von Plessen, F. Springer, A. Plech, *J. Chem. Phys.*, 124, (2006) 184702.

[3] V. Kotaidis, A. Plech, *Appl. Phys. Lett.*, 84 (2005) 213102.

[4] A Siems, S Weber, J Boneberg and A. Plech, *New. J. Phys.* 13 (2011) 043018.

[5] A. Plech, V. Kotaidis, M. Lorenc, J. Boneberg, *Nature Phys.* 2 (2006) 44.

[6] S. Ibrahimkutty, J. Kim, M. Cammarata, F. Ewald, J. Choi, H. Ihee, A. Plech, *ACS Nano* 5 (2011) 3788.

[7] A. Plech, S. Ibrahimkutty, D. Issenmann, V. Kotaidis, A. Siems, J.Phys.Conf. Ser. 425 (2013) 092008.

[8] X. Ye, et al., *Nano Lett.* 13 (2013) 765.

[9] E. Boulais, R. Lachaine, M. Meunier, *Nano Lett.* 12 (2012) 4763.

[10] E. Boulais, et al., *J.Photochem. and Photobiol.* C **17** (2013) 26.