ESRF	**Experiment title:** Metal nanorod photoexcitation – nonlinear excitation versus thermal process	**Experiment number**: SC4919
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Report:

Gold nanorods (in liquid phase) show a strong surface plasmon resonance (SPR) in the near infrared, which makes them an interesting tool for photonic and photo-thermal applications, in particular in the tissue window of biological material. Nevertheless, it has earlier been seen that strong photoexcitation with short laser pulses, while being able to raise particle temperatures by several hundreds to thousands of Kelvin, at the same time causes prominent and irreversible restructuring already after a single laser pulse. We have analysed the restructuring with high temporal and spatial resolution and drafted a reaction map as function of delay and laser fluence [1]. One main result shows that a transformation from rods (22 x93 nm) to spheres is nucleated at a fluence that is barely enough to create vapour bubbles that can be exploited in applications. The transformation starts already in the solid phase of the particles. At the same time, the caloric balance is not fulfilled, as the excitation density is much lower than what would be calculated from optical extinction. Therefore, we aimed for analysing the relation to the SPR and thus the question of nonlinear energy uptake, such as transient bleaching by varying the excitation wavelength around the SPR.

Experimental setup:

The suspension of several samples of gold nanorods with different aspect ratio was pumped through a closed capillary, which is intersected by the laser beam and the X-ray path. The liquid was only cycled once to avoid damage accumulation in the nanorods.
X-ray scattering is collected at two distances of the CCD of 120 mm and 650 mm to resolve both SAXS and WAXS. As the nanoparticles are randomly oriented in the liquid, the static scattering pattern in each case is rotationally symmetric. This changes, if nanorods are excited preferentially with long axis being parallel to the laser polarization. Then, the scattering pattern will display a anisotropy, if shapes are changing (SAXS) or crystal orientation of the (single-crystalline) particles is affected.

Data quality:

The experiment was running smoothly, so that we could map the fluence between approx. 5 and 1000 J/m^2 and the delay between 80 ps and 10 µs for comprehensively for 4 samples, each at 2 or 3 different wavelengths around the SPR. Additionally, 2 sets of spherical samples were analysed for comparison [2].

Results:

The results from an earlier experiment (SC3678 and [1]) could in general be reproduced. In particular, the anisotropy in the SAXS pattern allowed for pinpointing the onset of irreversible particle shape changes. The shape relaxation started after a delay of about 800 ps and lasted during the probed delays up to 10 µs. Selected SAXS difference maps are shown in fig. 1 together with results for the asymmetry as function of fluence for 2 samples at selected wavelengths.

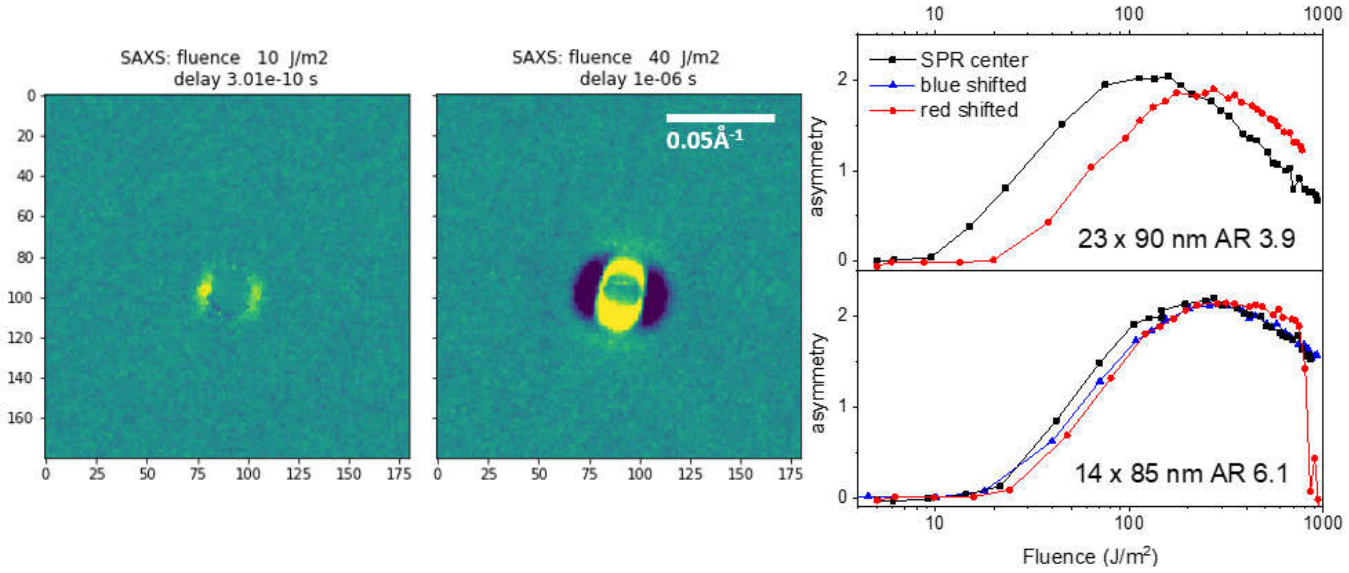

***Fig 1**: From left: difference SAXS pattern at a delay of 300 ps and 10 J/m^2; difference SAXS pattern at a delay of 1 µs and 40 J/m^2 (both for aspect ratio AR 3.9); Plots of the asymmetry of the SAXS pattern at 1 µs for two samples with aspect ratio AR of 6.1 and 3.9, respectively.*

At the center of the SPR resonance (850 nm for AR 3.9) we find that the threshold for shape relaxation is crossed already below 40 J/m^2, while at the wing of the SPR (920 nm) the threshold is shifted to higher fluence in the same amount as the extinction decreases. However, for nanorods with high aspect ratio (AR 6.1) no such change between the different wavelengths relative to the SPR is found. This points towards a ultrafast bleaching of the SPR within the pulse duration. Comparing to the sample with low aspect ratio the effects seems to be correlated to the particle shape. After analysing the complete data set we are looking forward to discuss the significance and correlate the behaviour with lab experiments.
Bubble formation at SPR (300 ps) is found to be as low at 10 J/m^2, slightly lower than observed before in blue-shifted excitation [1].
Such behaviour has been compared to spherical particles, which tends to relax into the same shape even after melting, but show fragmentation at considerably higher fluence [2].

Conclusions

The laser-induced structural dynamics of gold nanorods with different aspect ratio has been investigated as function of delay, fluence and excitation wavelength, which gives a more detailed insight into the mechanisms of structural instability.

References:

[1] A. Plech, S. Ibrahimkutty, S. Reich, G. Newby: *Thermal dynamics of pulsed-laser excited gold nanorods in suspension*, Nanoscale, 9 (2017) 17284-17292.
[2] A. Ziefuß, S. Reich, S. Reichenberger, M. Levantino, A. Plech: *Structural kinetics of picosecond laser fragmentation of suspended gold spheres*, Phys. Chem. Chem. Phys. (2020) early view. DOI: 10.1039/C9CP05202J