

Finding the best efficiency for laser-machining of gold colloids

A detailed understanding of the heating efficiency and property change of colloidal gold nanoparticles during the fragmentation process was missing. Using X-ray scattering, the local excitation efficiency of gold nanoparticles was examined on ultrashort timescales. Although the absorption efficiency is higher, the heating efficiency at the plasmon resonance of gold nanoparticles is significantly lower compared to the intraband excitation.

The synthesis of quantum-sized metal particles without any organic impurities can be achieved by laser ablation and laser fragmentation of matter in an inorganic, liquid environment [1]. However, in order to enable independent and flexible material design, which is required for the different demands of technological applications such as catalysis, the mechanisms and processes that occur during laser excitation, heating and structure transformations of nanoparticles need to be understood [2]. In this work, the excitation (heating) efficiency of gold colloids by laser pulses was studied with picosecond time resolution, and was compared for 532 nm under plasmon excitation and 400 nm at interband excitation with 1 ps laser pulses.

Plasmon excitation generally shows a higher ground state extinction and absorption (as seen in Figure 48), which is beneficial for resonant applications, where a very local strong electric field can be harnessed. The inset in Figure 48 additionally depicts an electron micrograph of the used nanoparticles with an impression of the near-field that is excited by the incoming polarised laser.

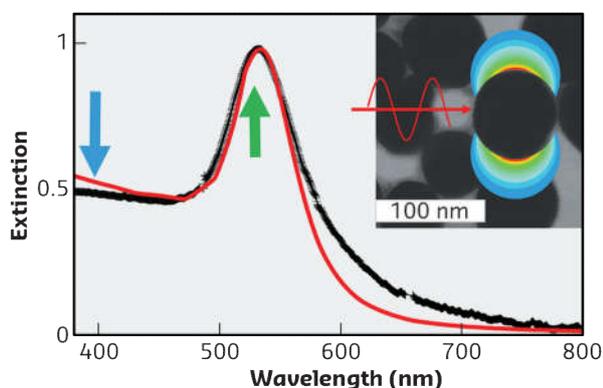


Fig. 48: Spectral extinction of a gold colloid of 53 nm particles in water from measurement (crosses) and calculation (line), together with the optical excitation wavelengths (arrows). The inset depicts some gold nanospheres together with the excited near-field distribution when illuminated by a linear polarised light source.

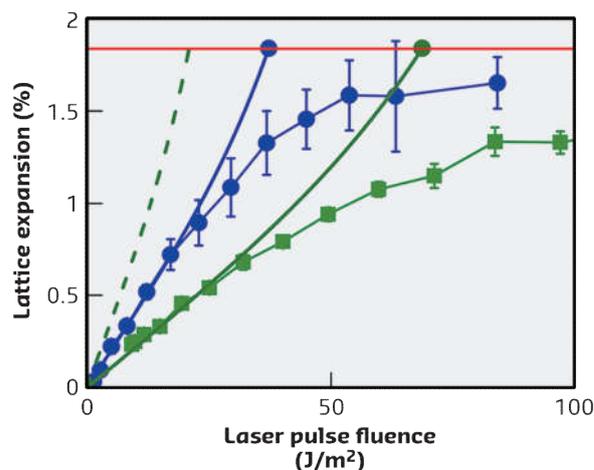


Fig. 49: Transient lattice expansion of the colloid as a function of applied laser fluence for 400 nm (blue symbols) and 532 nm (green symbols) laser pulses. The lines show the predicted expansion (dashed line for 532 nm) and the fitted expansion for both wavelengths.

It was found that the heating of the nanoparticles within several hundred picoseconds after laser excitation, despite the higher absorption efficiency at 532 nm (optical plasmon excitation), is considerably lower compared to an interband excitation at 400 nm. Hereby, the particle heating and temperature change, as well as the subsequent structure and size change of the laser-excited nanoparticles, was measured with the help of wide- and small-angle X-ray scattering, respectively, using the laser-pump-X-ray-probe setup at beamline ID09. At this setup, the transient state of the lattice expansion of colloidal gold nanoparticles can be caught with a 50 ps time resolution and be calorically (e.g., by the heating efficiency) compared to the incoming laser intensity.

Figure 49 shows the measured lattice expansion (interpreted as nanoparticle heating) at the two wavelengths and a pump-probe delay of 55 ps, together with a theoretical prediction including the gold expansion coefficient and latent heat. The lattice expansion is expected to stop at about 1.8 %, where the melting point of gold is reached, and the powder scattering should vanish. Indeed, the increase of the expansion follows the prediction with an onset of melting around 40 – 80 J/m². Yet, the expansion for 532 nm (green line in Figure 49) shows a much smaller slope than predicted by the absorption coefficient, indicating a lower heating efficiency despite the higher absorptivity.

The reason for this behaviour is currently hypothesised to originate from an ultrafast bleaching of the plasmon resonance due to non-equilibrium excitation, as well as yet-to-be-validated additional dissipation channels

due to the interaction of the near-field with the nanoscale environment. The study will enhance general understanding of how ultra-short laser pulses and

nanoparticles interact and how this interaction can be used to tune the properties of nanoparticles for future applications.

PRINCIPAL PUBLICATION AND AUTHORS

Low efficiency of laser heating of gold particles at the plasmon resonance - an X-ray calorimetry study, A. Plech (a), A.R. Ziefuss (b), M. Levantino (c), R. Streubel (b), S. Reich (a), S. Reichenberger (b), *ACS Photon.* **9**, 2981-2990 (2022); <https://doi.org/10.1021/acsp Photonics.2c00588>

In situ structural kinetics of picosecond laser-induced heating and fragmentation of colloidal gold spheres, A. Ziefuß (b), S. Reich (a), S. Reichenberger (b), M. Levantino (c), A. Plech (a), *Phys. Chem. Chem. Phys.* **22**, 4993-5001 (2020); <https://doi.org/10.1039/C9CP05202J>

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Temporal decoupling between lattice expansion and molecular spin transition observed with time-resolved X-ray diffraction

Time-resolved X-ray diffraction was used to investigate the photo-induced dynamics in microcrystals of a spin crossover iron complex. By tracking the molecular spin state and the structure of the lattice after laser photo-excitation, it is demonstrated that the volume expansion precedes the thermo-elastic spin transition in this prototypical system for molecular cooperativity.

The general excitement born out of the ability to access the ultrafast time scales has caused a rush of new ideas, new materials and new instruments. There is clear evidence now that materials can be directed between different macroscopic states by using electronic or phononic excitations. One feat in particular has attracted a lot of effort, namely the control of materials with an ultrashort laser pulse, on pathways unattainable at thermodynamic equilibrium. Recent studies utilising time-resolved optical spectroscopy [1] revealed a size-dependent spin-state switching time and sparked the expectation that transition-metal compounds would obey the rule “the smaller the faster”, owing to a positive elastic feedback from the expanding lattice on the volume-changing molecules. At equilibrium, both the unit cell volume and the concentration of high spin molecules show correlated jumps upon the phase transition from low- to high-spin state at 165 K.

In this work, 100-ps X-ray diffraction was synchronised to a 1-ps pump laser exciting a charge transfer state to probe the photo-induced dynamics of an Fe(III) compound. The experiments were performed at beamline ID09 in quasi-grazing reflection geometry at 0.2° incidence angle to enhance the signal from the thin film sample and reduce diffuse background from a bulky substrate (Figure 50).

A quantitative structural analysis [2,3] at several time delays allowed to establish a sequence of events in the non-equilibrium dynamics. Interestingly, this material exhibits a very different behaviour from the insulator-to-metal transformation dynamics of an inorganic semiconductor upon propagation of laser-induced, long-range deformations [4]. In the latter case, the phase