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Light-induced structural phase behaviour of metal nanoparticle materials

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Abstract. We have investigated the structural dynamics of gold nanoparticles induced by femtosecond light excitation. Structure evolution in both embedded particles (glass matrix or liquid water suspension) and quasi-free particles adsorbed on a solid surface is analyzed. By use of stroboscopic laser pump- x-ray probe techniques the structural relaxations have been resolved on the 100 ps time scale at the European Synchrotron Radiation Facility. Several methods including powder scattering, liquid scattering and small angle scattering serve to resolve microscopic and mesoscopic length scales of the composite system. The thermal response includes the heating, lattice melting, explosive solvent evaporation and solvent cooling subsequent to the laser flash excitation. Nonthermal effects are observed with femtosecond excitation. They are attributed to ablation from the particle and particle explosion at strong nonequilibrium conditions. The observations can form a complete picture of the energy dissipation and phase transitions involved in nanoscale composites.

1. Introduction
Optical properties of nanoparticles and nanoparticle composites including nonlinear optical response are widely studied and well understood [1, 2]. Optical excitations in metal nanoparticles include the response of the conduction electron system, especially the plasmon resonance, which provides a channel for ultrafast energy transduction. While it is known, that ultrafast and strong nonequilibrium excitation induces important structural relaxations, less information is available on this aspect, where studies have concentrated on the electron phonon coupling and vibrational properties due to size confinement, mostly studied by laser pump-probe spectroscopy [3, 4, 5, 6]. An attempt to resolve the melting process has been reported, where the shape transformation served as indicator for the lattice melting [7]. By use of x-ray scattering methods, the structural relaxations in condensed matter, and in particular in nanoscale systems are directly accessible. We have reported the ultrafast heating of silver and gold particles [8, 9], the determination of lattice temperatures and melting in gold sols [10] and the reaction of the water medium upon the energy flow [11].

2. Materials and methods
The time resolved scattering experiments on the nanoparticle composites have been performed at the beam port ID09B at the ESRF [12]. A femtosecond regenerative Ti:Sapphire amplifier system (Coherent MIRA, Spectra Physics Hurricane) has been synchro-locked to the radio frequency of
the electron storage ring. Thus the emission of laser pulses is time locked to the pulse train of emitted x-rays from the storage ring. A 235 pole undulator of 17 mm period produces intense x-ray pulses at a center wavelength of 15 keV. They either pass through a channel-cut silicon monochromator in order to achieve an energy resolution of $1.4 \times 10^{-4}$ or are guided directly to the sample after further opening the undulator gap and optimizing heat load, spectral purity and achievable momentum transfer [13].

The matching of the x-ray repetition frequencies to the laser firing at 986 Hz is achieved by a mechanical chopper, which is synchronized to a fixed electron pulse in the ring. The delay between laser and x-ray pulses can be varied in steps of 5 ps over a millisecond range. The electronic jitter is much smaller than the x-ray pulse length of 80-110 ps (16 bunch mode). The calibration of coinciding laser and x-ray pulses (delay $\tau = 0$) is done by the onset of photo signals as seen in the inset of figure 1, to a precision better than 20 ps. This setup allows one to apply pump-probes schemes as known from femtosecond spectroscopy except that a two dimensional x-ray detector can be used to record the reciprocal space at atomic scale resolution.

The laser power is controlled by a combination of a $\lambda/2$ retarder and a Glan laser prism and calibrated with a laser power meter (Coherent). The 150 fs pulses at 800 nm from the regenerative amplifier are frequency-doubled to 400 nm and used for sample excitation.

Gold nanoparticles have been synthesized by the well known citrate method [14]. We control the sizes of the particles by varying the relative concentrations of gold ions with respect to the citrate reductant, which serves also as stabilizer. The size distribution is found to be within 12 % - 18 % depending on particle size and calibrated by SEM, SAXS measurements and optical extinction spectra. The sols have a rather high gold concentration (0.8 - 1.2 mM) and can be directly used for the photo excitation studies, when pumped through a 300 $\mu$m borosilicate capillary and illuminated by coaxial x-ray and laser pulses. They have also been adsorbed onto a solid surface of float glass in submonolayer coverage. This technique uses the established electrostatic self-assembly processes, as developed for aqueous polyelectrolyte adsorption [15]. As final step a thin layer of waterglass (sodium waterglass, Roth Chemicals) can be spin coated on top followed by an annealing step at 200 °C. This results in a solid glassy layer of roughly 20 $\mu$m, in which the particles are embedded.

For the powder scattering from the particle lattice a series of images at various delays are collected. A careful normalization and subtraction of the background is necessary, the powder scattering distributed in Debye-Scherrer rings, is usually within a 1-10 % range of the background. The resulting peaks are fitted by appropriate functions, typically single or multiple Lorentz functions. The peak positions (mainly of the (111) reflection) serve to derive the lattice parameter. Integrated intensity and peak width are important for the determination of lattice strain and melting.

SAXS and liquid scattering are recorded with the polychromatic x-ray pulses at different sample-detector distances (630 mm and 60 mm). As the relative photoinduced signal in these measurements is extremely weak ($10^{-4}$ to $10^{-2}$) compared to the background (scattering from the capillary, liquid and air) a set of interleaved exposures has to be taken, where once the x-ray pulse arrives before the laser pulse (serves as unperturbed reference) and at variable delay after laser excitation. The CCD images are then subtracted from each other after proper normalization to remove drifts, corrected for polarization, space angle intensity and integrated azimuthally to derive the difference photosignal $\Delta S(Q, \tau)$ where $Q = 4\pi/\lambda \cdot \sin(2\Theta/2)$ denotes the scattering vector as calculated from the scattering angle $2\Theta$ [16].

3. Linear response of the nanoparticles composites: Heat dissipation, melting and water evaporation
The phonon excitation from a heated electron gas as modeled by the two temperature model of the coupled electron and phonon gas is a relatively fast step, which occurs within 2-5ps [17, 18, 2].
With our standard setup it cannot be resolved in time. The shortest available pulses (at low bunch current in the storage ring) of 75 ps FWHM still show a resolution limited rise of the lattice parameter after laser excitation [19].

After the initial fast heating of the lattice a relaxation appears that strongly depends on size and contact medium of the particles. In general the cooling times scale with the ratio of volume to surface of the particles, i.e. with the radius, by an interplay between stored energy and cooling efficiency [20, 5]. Therefore particles on a free surface show very long relaxation times up to 13 ns, seen in figure 1 a) for 102 nm particles, in comparison to 35 nm particles with 750 ps. Covering these particles by a glass layer drastically reduces the cooling time as is expected for the increased thermal contact area (850 ps for 85 nm particles).

A quantitative calculation is possible, when taking two mechanisms of heat resistance into account, the finite conductance across the interface particle-medium and the heat diffusivity in the bulk medium. Silver particles in glass have shown a predominance of the interface conductance G, probably because of the nonideal physical contact, with G= 190 MW/m²/K [8], whereas for gold particles in water the diffusivity in the water phase is more important, with G= 105 MW/m²/K [10]. The fits are presented in figure 1 (b) for two particles sizes.

\[
g = 190 \text{ MW/m}^2/\text{K} \quad \text{(silver particles in glass)}
\]

\[
g = 105 \text{ MW/m}^2/\text{K} \quad \text{(gold particles in water)}
\]

This energy relaxation can be regarded as a general description, which is to first approximation not explicitly temperature dependent. The dynamics change completely when discontinuities of the condensed phase, such as phase transitions, are involved. One transition is the liquid vapor transition of water in the case of gold suspensions. It has been found that structural transients in the water phase occur at high excitation density [21, 11]. At the same time the heat transfer collapses at a threshold value of the excitation density and the cooling rate of the particles is reduced [22].

The structural transients in the water phase indicate a bulk compression that is caused by the formation of vapor bubbles close to the particles, which grow and then vanish on the nanosecond time scale. The vapor formation is not caused by normal boiling, but by explosive evaporation close to the water spinodal temperature [23] due to the large heating rate that locally exceeds \(6 \cdot 10^{12} \text{ K/s}\).
observed, but for a higher particle temperature above $T_m$.

Figure 2. Liquid scattering changes of the water phase after laser excitation as function of scattering vector $Q$. The laser power was 5 times the melting threshold. From bottom to top: 50ps, 250ps, 1ns, 5ns, 2µs compared to the static differential $dS/dp|_{T}^{(+)}$ with equal modulations. The marks indicate dips caused by Bragg scattering disappearance. The inset shows the amplitude of the signal as function of delay.

Secondly the excitation kinetics can be intercepted by the melting transition of the crystalline particles, as evidenced by the vanishing of the Bragg scattering [10]. It is found that after a cooling step the particles partially recrystallize. Yet the melting transition is not fully resolved with the cooling times (figure 3) indicating the existence of supercooled liquid particles in the solution. In addition the Bragg peak at the microsecond time scale in figure 3 is not fully restored which shows that the particles partially recrystallize. However, the transition point is much larger than the cooling step. The particles recrystallize. In addition the Bragg peak at the microsecond time scale in figure 3 is not fully restored which shows that the particles partially recrystallize. However, the transition point is much larger than the cooling step. The particles recrystallize. In addition the Bragg peak at the microsecond time scale in figure 3 is not fully restored which shows that the particles partially recrystallize. However, the transition point is much larger than the cooling step.
Laser power [mW]

peak area

Figure 4. Maximum observed lattice expansion for 100nm particles in water (left) and 150nm particles on a surface (right) together with a calculation of the expected thermal expansion as function of laser power. The upper panels show the intensity of the (111) reflection as function of laser power together with a calculation of the Debye-Waller factor. Melting is expected at 29 mW for the gold sol. Full symbols are used for single shot excitation, open symbols for multiple shots on the same particles. The lower panels show the scattering intensity as a function of laser power, together with a calculation of the expected lattice expansion for gold particles in water (left) and 150nm particles on a surface (right).
vanishes completely at the melting point. The supported particles however show a very narrow interval of linear expansion, above which no further expansion is recorded. This is accompanied by the nearly complete loss of scattering intensity. The particles have lost their crystallinity and probably their shape as well. An indication is the SAXS signal from the debris appearing at low Q in figure 2. The destruction of the particles forms a serious limitation for applications, which rely on reversible processes. It can, on the other hand, be an interesting mechanism for controlled manipulation and structuring of nanoscale material. The quantitative understanding of the interplay of energetic relaxations and structural response is important for nanophotonic materials applications.

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