

# Holographic Grating Formation in Silver Nanoparticle Suspensions

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**Abstract:** Thermal gratings are recorded in silver nanoparticle suspensions by nanosecond pulsed holography. Initial transients in diffraction efficiency demonstrate competing effects in grating formation. The grating's final decay is consistent with the suspension's thermal conductivity.

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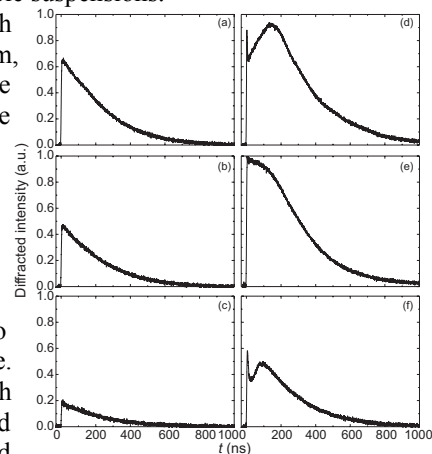
OCIS codes: (090.7330) Volume holographic gratings, (160.4330) Nonlinear optical materials

Colloidal suspensions of metal nanoparticles have been intensely studied due to their interesting thermal and nonlinear optical properties. The high third-order nonlinearity of metal nanoparticles at wavelengths close to the surface plasmon resonance makes such suspensions materials attractive for optical switching applications [1]. In addition, strong refractive index changes can be induced on the nanosecond timescale due to the absorption of the nanoparticles. The reconfigurable nature of liquid suspensions of nanoparticles allows for a wide range of potential applications [2]. However, the optical response of these materials is still not completely understood, especially at the nanosecond time scale [3]. In this paper, we report on the nanosecond time dynamics of gratings recorded in silver nanoparticle suspensions.

Spherical silver nanoparticles suspended in toluene, with mean diameter of  $\sim 3.8$  nm and a resonant absorption peak at 433 nm, were synthesized following Collier et al. [4]. The suspensions were diluted to produce samples of varying absorption. Holograms were recorded using frequency doubled Nd:YAG laser pulses at 532 nm (intensity up to  $I=10$  GW/m<sup>2</sup>, pulse duration  $\tau = 6$  ns FWHM, beam diameter = 6 mm, s-polarized). The samples were contained in a quartz cuvette 10 mm wide and 4 mm deep, and had optical densities between 1.1 and 0.2 at the recording wavelength.

Gratings were written by separating the pump pulse into two equal intensity parts, which overlap at the center of the cuvette. The propagation directions of the two pulses were symmetric with respect to the optical axis, and the angle between them was varied to produce interference fringes with periods between 1  $\mu$ m and 2.5  $\mu$ m. A Bragg matched continuous wave laser at 785 nm (2 mm beam diameter, s-polarized) was used to probe the recorded grating, and the +1 diffracted order was detected using a PIN diode with a 1 ns rise time. Each experiment was conducted with more than a minute between pulses, in order to allow the suspension to return to thermal equilibrium. No change in the absorption of the samples after exposure was observed, indicating the nanoparticles did not experience agglomeration or shape change in the course of the experiment.

We examined the effect of both nanoparticle concentration and pulse intensity on the grating dynamics. The initial evolution of the diffracted signal is highly dependent on both concentration and intensity (see fig. 1). The final decay of the signal can be fitted in all cases with a single monoexponential function. This is consistent with the theory for the decay of a thermal grating in continuous media with an amplitude given by  $\Delta T = \Delta T_0 \exp(-t/\tau_{th})$  and a time constant  $\tau_{th} = A^2/(4\pi\kappa)$ . Here  $A$  is the fringe period of the grating, and  $\kappa$  is the thermal diffusivity of the medium [5]. The calculated time constants of experiments conducted at different fringe spacings produce a curve that is well described by a quadratic function (fig. 2). Here,  $\tau$  should be twice the value of  $\tau_{th}$ , since the diffracted intensity is proportional to the square of the temperature change for small  $\Delta T$  [5]. From the fit of the quadratic curve, we find the thermal diffusivity  $\kappa$



**Fig. 1: Diffracted intensity vs time at different particle concentrations. Pulse intensity is 4.6 GW/m<sup>2</sup> for (a,b,c) and 10 GW/m<sup>2</sup> for (d,e,f). Absorption is OD 1.1 in (a),(d) OD 0.55 in (b),(e), and OD 0.22 in (d),(f).**

$= 7.27 \times 10^{-8} \text{ m}^2\text{s}^{-1}$  which is in good agreement with the literature value of thermal diffusivity of toluene  $8.85 \times 10^{-8} \text{ m}^2\text{s}^{-1}$ . Although the final behavior of the thermal gratings is well described by the above analysis, the earlier transients imply other effects are present in grating formation.

The data shown in fig. 1 are representative of the trends observed in all of our experiments. At low power (fig. 1 (a),(b), and (c)) there is a 6 ns rise time (well correlated to the pulse width) followed by a monoexponential decay. This is consistent with a simple thermal grating. However, at higher powers other transients appear. At the lowest concentration, the initial rise is followed by a steep dip, and then another rise followed by an exponential thermal decay. At intermediate concentrations, the dip disappears. At the highest concentration, the initial rise has a narrower width of around 3 ns, and higher peak diffraction due to the delayed rise. The narrower initial peak could be due to a non-negligible instantaneous Kerr effect at higher intensity; however, the Kerr effect should only be acting during the presence of the pump pulses (the first six nanoseconds of the signal). There must be thermal effects that are only present at higher concentrations and powers to account for the behavior of the second transient.

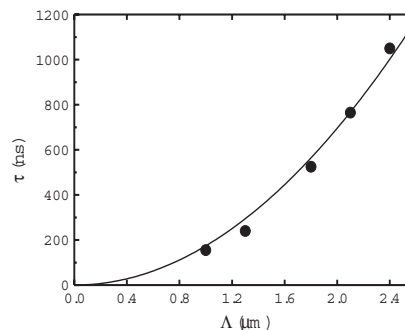
Heating of the solvent leads to thermal and thus negative changes of the refractive index. It has been shown that the heat transfer from nanoparticles excited by nanosecond pulses to the solvent can last for several tens of nanoseconds. This behavior is strongly influenced by both particle size and concentration [3]. The diffusion of thermal energy into the solvent could be the mechanism responsible for the discrepancies in the temporal evolution of the first peak and valley. Since energy is only absorbed by the nanoparticles, it will take time for the heat released into the solvent to form a continuous temperature grating. As the concentration increases, heat generated at neighboring nanoparticles may influence the rate of heat transfer from a particle into the solvent. This may account for the peak diffraction efficiency appearing later at the highest concentrations.

Another explanation may be possible: The absorbed energy may be sufficient to boil a small shell of the solvent around each nanoparticle, thus leading to strong refractive-index changes, resulting in a change of the surface plasmon resonance and in light scattering at the phase boundary in the solvent [6].

In either case, there are at least three effects that influence the strength of the diffracted grating signal: the instantaneous Kerr effect (a positive refractive index change), a simple thermal grating such as those seen at lower power (a negative refractive index change) and a shorter lived delayed grating arising probably due to the thermal changes in the particles and the solvent. Further investigation may allow us to determine the parameters of these effects.

In conclusion, we have shown that transient signals appear in gratings recorded in suspensions of silver nanoparticles using nanosecond pulses. In addition to an instantaneous response and to further effects occurring just after the pulse illumination, also a longer-lasting thermal grating has been verified. The shorter time scale behavior of gratings recorded at high intensity may be an interesting probe into the dynamics of heat transfer at the nanometer and nanosecond scales.

We gratefully acknowledge support from Deutsche Telekom AG, the DFG, and the DARPA Center for Optofluidic Integration.



**Fig. 2: Diffracted signal decay time vs. fringe spacing**

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