Ultrafast Optical Nonlinearities of Single Metal Nanoparticles

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Abstract. We have measured nonlinear scattering from plasmons in individual Au nanorods and have correlated second-harmonic activity of Ag nanoparticles and clusters to morphology. The measurements reveal novel ultrafast nonlinear phenomena related to electron confinement and enhanced plasmon dephasing.

1. Introduction

Light can couple strongly to coherent oscillations of conduction electrons in Au and Ag nanoparticles, known as surface plasmons [1]. Resonant excitation of these plasmons with ultrafast laser pulses readily results in very large nonlinear optical responses [2,3]. These nonlinearities may find important application in functional plasmonic devices, such as high-speed, all-optical, nanoscale switches. Moreover, the physical mechanisms responsible for the plasmonic nonlinearities are related to the nanometer-scale dimensions of the particles and are thus different from the mechanisms responsible for bulk optical nonlinearities. Understanding these novel material nonlinearities requires the ability to excite the metal particles on resonance with their plasmon frequencies and probe the subsequent ultrafast dynamics, and to relate the measured response to the nanometer-scale structure of the particles. This, in turn, requires the isolation of individual nanoparticles and nanoparticle aggregates, in order to remove the obscuring effects of inhomogeneities in particle size and morphology.

We have made the first measurements of nonlinearities in ultrafast resonant scattering of light from plasmons in single Au nanorods [4]. We observe an unexpected saturation of the response under strong excitation due to an increase in the plasmonic damping rate. We have also measured second-harmonic (SH) activity from single Ag nanoparticles and nanoparticle clusters and have correlated this activity to high-resolution imaging of particle morphology by transmission-electron microscopy (TEM) [5]. The measurements indicate that SH activity is strongly enhanced for resonant excitation of longitudinal plasmons. In both cases, the measured response is attributable to the restriction of coherent plasmon oscillation by the nanorod surfaces.

2. Ultrafast nonlinear scattering from single gold nanorods

Our ultrafast (interferometric) nonlinear spectroscopic studies of plasmons involve single Au nanorods that are chemically synthesized using a seed-mediated growth process [6]. The sample consists of sparsely dispersed rods, bound to a glass coverslip, and is measured using total-internal-reflection microscopy. Single rods are identified by exciting with incoherent white light and measuring the scattering spectrum, comparing this to calculation, and measuring the polarization dependence of the scattering.

Nonlinearities of the single nanorods are measured using an equal pulse correlation interferometric pump–probe technique. The rods are excited with 20fs pulses from a mode-locked, cavity-dumped Ti:Sapphire laser, which are split into two equal-intensity parts and focused to a common spot on the sample. For delays between the two pulses that are shorter than the pulse duration, the measured scattering signal exhibits an interference pattern, shown in Figure 1. The asymmetry of the amplitude of this interference pattern is a measure of the ultrafast nonlinearity in scattering from the single nanorod and can exceed 20% at high laser intensities. The diminishment is a decrease in the scattering cross-section.

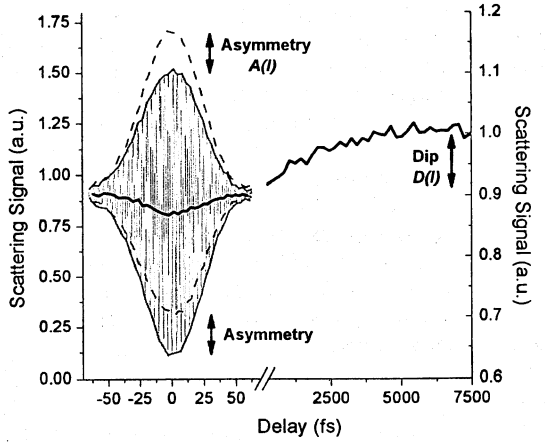

Fig. 1. Single-rod scattering signal as a function of delay between two laser pulses. Left: scattering signal for overlapping (47pJ) pulses (light line); envelope of interference pattern (solid line); the same envelope, inverted around the average scattering signal at a delay of 75 fs (dashed line); and average of upper and lower envelopes (heavy line). Right: scattering intensity for non-overlapping (94pJ) pulses.

When the delay between the laser pulses is increased such that the pulses no longer overlap, the scattering signal exhibits an increase over a time scale of a few picoseconds, as shown. The response is characteristic of the heating of conduction electrons by the laser pulse, followed by their cooling and equilibration with

lattice phonons [2]. The data for several rods and for a range of pulse energies are well fit to an electron heating model. Our field-resolved 4WM measurements corroborate these relaxation timescales [7].

Unexpectedly, this same thermal model also quantitatively explains the measured nonlinearities on sub-20fs time scales, indicating that a nearly thermal distribution of electrons is produced in the rod within a time that is short compared to the 20fs laser pulse duration. This interpretation is further supported by a measurement of intensity-dependent scattering spectra using a single laser pulse: the single-nanorod plasmon resonance shows a broadening and red-shift consistent with ultrafast creation of high-temperature electrons. The absence of any measurable coherent nonlinearity, and the "instantaneous" emergence of an incoherent thermal nonlinearity, indicate that the strong, resonant laser excitation increases the plasmon damping rate and destroys its coherence. This results in an effective saturation of the plasmonic response on the 20fs time scale, which is consistent with resonant transient-extinction measurements on nanorod ensembles under strong excitation conditions [7].

The loss of electron coherence may be due to the effects of the nanorod boundaries. For large laser powers, the amplitude of electron oscillation reaches as much as 8% of the rod length, resulting in a significant compression of the electron gas at the rod surfaces. This electron "pile-up" can induce plasmon damping through multi-particle interactions, such as coupling of plasmons to single-electron excitations and enhanced nonlinear optical signals [5,8].

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