Ultrafast optical nonlinearities of metal nanoparticles: Single-particle measurements and correlation to structure

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\textbf{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. Surprisingly, the coherent plasmon response is suppressed relative to the hot electron response indicating enhanced plasmon dephasing. In a parallel set of studies we demonstrate nanometer scale localization of the nonlinear optical response of single nanoparticles and aggregates and correlate this with their morphology. Position markers are fabricated on an optical and electron-transparent substrate (Si$_3$N$_4$ thin film) that allows optical measurements and transmission electron microscopy (TEM) imaging of the identical nanoparticles or aggregates. The second harmonic (SH) activity optical image of individual Ag nanostructures is registered with the TEM image. Centroid localization of the optical signals allows correlation with better than 25 nm precision. This is sufficient to determine the origin of optical “hot spots” within multi-particle aggregates.

\textbf{Keywords}: nonlinear optical, ultrafast optical, single molecule, nanorod, nanomaterials

\section{1. INTRODUCTION}

Understanding the structure-property relationship of nanoparticles and tailoring their optical and electronic properties is a prerequisite to designing novel nanomaterials.\cite{1} “Bottom-up” fabrication of novel functional materials based upon nanoscale building blocks (nanoparticles or nanocrystals) is being extensively pursued.\cite{2-8} The dimensions of such nanocrystals (typically 2-100 nm) lie between bulk crystals and single molecules. Quantum or classical electron confinement effects give the nanocrystals unique properties that are fundamentally different from their bulk or atomic cluster counterparts.\cite{8-10}

The linear and nonlinear optical properties of metal and semiconductor nanocrystals are of particular interest for optical and biosensing applications.\cite{11,12} Most previous studies examined bulk properties of nanoparticle solutions, such as linear scattering and second harmonic (SH) generation.\cite{3,4,13-15} These ensemble measurements provide information averaged over the nanoparticle size and morphology distributions, and thus, the precise structure-property relationship of individual nanoparticles is obscured. Therefore, single particle measurements are necessary to gain a deep and complete understanding of their optical properties and those of individual particle aggregates.\cite{16-23}

Light can couple strongly to coherent oscillations of conduction electrons in Au and Ag nanoparticles, known as surface plasmons.\cite{24} Resonant excitation of these plasmons with ultrafast laser pulses readily results in very large nonlinear optical responses.\cite{25,26} 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.\cite{27}
We have made the first measurements of nonlinearities in ultrafast resonant scattering of light from plasmons in single Au nanorods.[28] 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).[29] 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.[28, 30] 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 measurement. The rods are excited with 20-fs 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 indicates a decrease in the scattering cross-section as a result of the third order response opposing the sign/phase of the linear scattering.

![Fig. 1](image-url)  

**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 red line); the same envelope, inverted around the average scattering signal at a delay of 75 fs (dashed red 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.[25, 28] The
data for several rods and for a range of pulse energies are well fit to an electron heating model. Our comparative field-resolved 4WM measurements corroborate these relaxation timescales.[31]

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 short compared to the 20-fs 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 20-fs time scale, which is consistent with resonant transient-extinction measurements on nanorod ensembles under strong excitation conditions.[31]

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.

3. STRUCTURE-DEPENDENT SECOND-HARMONIC ACTIVITY OF SILVER NANOPARTICLES

A complementary set of experiments involve the ultrafast nonlinear microscopy of individual Ag nanoparticles and nanoparticle aggregates. [10,29] We have developed an approach that permits correlation of SH activity with nanoparticle morphology imaged by TEM, based on the fabrication of reference markers on a thin Si3N4 substrate that is transparent to both light and electrons. We investigate the SH activity of single Ag nanoparticles and clusters, including dimers and trimers that form spontaneously through the deposition of colloidal Ag nanoparticles, under excitation with ultrafast laser pulses. Measurement of the emission spectrum and power dependence are used to confirm the SH nature of the collected signal.

As shown in Figure 2, trimer structures (#s 6 & 10) exhibit the strongest SH response, followed by dimers (#s 4, 5, 7, & 8) and single spherical particles (#s 9 & 12). On the other hand, aggregates with more than three particles (#s 6 & 10) are not necessarily more active than dimers, while single nanorods (#s 2 & 11) are highly active. The SH excitation spectra of a dimer and a nanorod show narrow peaks centered at 850 nm and 860 nm, respectively, corresponding to the expected resonance wavelengths for longitudinal plasmons.[24,27,32] In addition, the SH activity is maximum when the incident laser light is polarized along the long axis of the dimer or nanorod. In other words, the SH response is due to a nonlinearity in the polarization created by resonant excitation of longitudinal plasmons; this response is enhanced by the large local field associated with the plasmon oscillation.

The mechanism for the observed resonant SH activity may also reflect the effects of the nanorod surfaces/boundaries. At high optical intensities, the bounding of electron motion causes a pile up of electrons near the nanoparticle boundaries resulting in a highly asymmetric electron distribution at the turning points of the plasmon oscillation. The anharmonic response would break the inversion symmetry of the nanorod, allowing the efficient generation of harmonics of the driving frequency.[33]
4. LOCALIZATION OF SHG AND CORRELATION WITH STRUCTURE

A bright field image and SH map of the marked area of the sample were acquired with white light (i.e., halogen) condenser illumination and the femtosecond near-IR laser pulse excitation, respectively. The images typically covered 35x35 µm square areas (on the order of the entire marker bar pattern). ImageJ was used to crop a specific area of interest, typically 5x5 to 10x10 µm square, that corresponded to the TEM image of the same area. Individual Ag nanoparticles and SH signals were then identified in both images. This allowed direct particle to SH emission correlation.

To transcend simply identifying particles and allow precise colocalization of emission and morphology, SH images were mathematically registered to their TEM image counterparts.[10, 29] The procedure is based on a simple point-to-point matching correlation and transformation. Briefly, centroids of hexagonal-arrayed spherical markers were determined from the TEM image. Next, localization of the marker SH emission was accomplished by either fitting a 2D Gaussian to the SH signal or when that failed due to low signal-to-noise ratio, determining the centroid. The Matlab “cpselect” tool was used to determine starting points for the localization. Optimization of the analysis parameters (box size, box center, convergence criteria) was done by hand. The set of corresponding marker points was then used to solve for a linear conformal transformation matrix $T$ relating the SH to the TEM coordinate space.

$$I_{\text{TEM}}(x', y') = T I_{\text{SHG}}(x, y)$$

(1)

$$T = \begin{pmatrix} s \cos(\theta) & -s \sin(\theta) \\ s \sin(\theta) & s \cos(\theta) \\ t_x & t_y \end{pmatrix}$$

(2)
The transformation $T$ allows scaling ($s$), translation ($t_x, t_y$), and rotation ($\theta$) and so avoids the complications of polynomial fitting or local image warping that would not fit the entire image. Consequently, no severe imaging aberrations must be present in the TEM and SH images. This condition is true for the small 10x10 µm areas that were carefully analyze in this work. The process was iteratively repeated until a satisfactory transform was found that successfully and simultaneously correlated all TEM and SH markers. This could be automated by minimizing goodness-of-fit parameters.

When the registration transform was determined, localization of the other SH emission features were then performed as above. These centroid coordinates were then transformed into the TEM image space and plotted. Additionally, the entire SH image was transformed and overlayed with the TEM image in ImageJ. The error of the image registration and correlation is estimated to be 25 nm and is limited by the size and structural irregularity of the 100 nm markers. As an example, Figure 3 compares the TEM image (Fig. 3a), the SH emission (Fig. 3b) and a detailed view of aggregate #1 with the arrow pointing to the centroid of SH emission (Fig. 3c).

5. CONCLUSIONS

The direct determination of nanoparticle structure and the correlation of this structure to optical activity has thus allowed a new insight into the nonlinear response of metal nanoparticles. It allows correlating and localizing the optical response of single nanoparticles or aggregates with TEM imaging of particle morphology and this enables determining the origin of optical “hot spots” within multi-particle aggregates. This technique can readily be adapted for other single-particle studies, such as surface-enhanced Raman scattering (SERS), potentially allowing insight into the fine structure of “hot spots” that exhibit enormous Raman enhancement, and ultrafast pump–probe single-particle studies.

REFERENCES