Femtosecond Response of a Single Metal Nanoparticle

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Received December 6, 2005; Revised Manuscript Received January 12, 2006

ABSTRACT

The ultrafast nonlinear optical response of a single metal nanoparticle is investigated by combining a high-sensitivity femtosecond pump–probe setup with a spatial modulation microscope. Experiments are performed on 20 and 30 nm silver nanospheres, in situ characterized via their optical linear extinction spectrum. The measured transient response permits investigation of the electron–phonon energy transfer time in a single nanoparticle. Its dependence on the electronic temperature is quantitatively interpreted using the two-temperature model.

Time-resolved femtosecond spectroscopy has been extensively used to investigate the ultrafast nonlinear optical response and the correlated electronic and vibrational kinetics of nanoparticles and nanomaterials. In particular, it constitutes a powerful tool for analyzing electron interaction processes and their modification by size reduction in metal nanoparticles.1–4 Most of these experiments were performed on large ensembles of particles dispersed in a liquid or solid matrix, with the concomitant difficulty of nanoparticle size, shape, and environment fluctuations. In the case of nanospheres, this has been circumvented by using high-quality samples with weak size and shape dispersions and performing experiments in environment independent conditions (i.e., for weak excitation of the particles).5,6 However, precise investigation of the impact of the particle shape and environment on the electron response requires the development of femtosecond spectroscopy of single identified nanoparticles.

Numerous time-resolved investigations of single metal nanoparticles of nanostructured metal surfaces rely on combining a specific optical detection scheme with a femtosecond spectroscopy setup.7–12 In the case of nanoparticles, near field optical microscopy has been recently extended to the femtosecond investigation of large gold nanorods (180 × 30 nm),7 using an approach similar to that developed for semiconductor nanostructures.13,14 The inherent difficulty of these experiments is making development of far field techniques particularly interesting. Though their spatial resolution is smaller, single nanoparticles can also be addressed using dilute samples. Transient single nanoparticle scattering and absorption have thus been detected in large nanospheres (diameter larger than 50 nm) with picosecond resolution.8,9 Scattering-based methods have recently been extended to the femtosecond domain in 80 nm gold nanospheres10 and in nanorods.11 As, for small nanoparticles, absorption dominates over scattering, transient absorption has to be monitored to address smaller particles (the ratio of the absorption to scattering cross sections scales as the particle volume). We report here on the first femtosecond investigation of the transient absorption of a single small metal nanoparticle (size smaller than 50 nm), coupling our recently demonstrated far-field spatial modulation spectroscopy technique15 with a high sensitivity pump–probe setup. This approach permits both to identify the studied particle via its linear extinction spectrum and to detect its ultrafast response, yielding information on the electron–lattice energy exchange in a single nanoparticle down to 20 nm size.

Experiments were performed in single silver nanospheres deposited on a cover glass. The samples were prepared by spin coating a colloidal solution in the presence of a polymer (poly(vinyl alcohol)). Two solutions with a mean diameter of 20 or 30 nm and a size dispersion of ±5 nm were used. With proper choice of the deposition conditions, very diluted samples were obtained, with less than one particle per μm². The single particle under study was first identified by measuring its extinction spectrum using the spatial modulation spectroscopy technique.15,16 This is based on periodically modulating the position of a nanoparticle in the focal spot of a laser beam of wavelength λ tightly focused by a 100× microscope objective. The resulting modulation of the transmitted power is detected by a lock-in amplifier. Its amplitude is imposed by the nanoparticle extinction cross section, σ_{ext}(λ), whose absolute value can thus be precisely determined. This setup permits detection of an absorbing nanoobject with an absorption cross section down to a few nm², yielding a detection limit of 2 nm for silver nanospheres.15

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the ensemble measurements performed in the colloidal
and narrowed surface plasmon resonances, as compared to

\[ \frac{\sigma_{\text{ext}}}{\sigma_{\text{sc}}}(\lambda_R) \text{ values of the}
\]

measured, comparison of the computed and measured spectra
permits precise characterization of the studied single nano-
particle and, in particular, determination of its volume.\textsuperscript{16}
Actually, already for \( D \approx 20 \text{ nm} \) silver nanoparticles, the
retardation effect influences the spectrum and has to be taken
into account. It corresponds to including multipolar terms
in the Mie theory (up to the 11th order in the present study).
For the two particles of Figure 1 we obtain \( D = 21 \) and 30
\text{ nm}, using the bulk \( \epsilon \) values measured by Johnson and
Christy.\textsuperscript{18} For these particles, absorption dominates over scattering, the cross-section ratio
\( \sigma_{\text{ext}}/\sigma_{\text{sc}} \) at \( \lambda_R \) being about 10 for the former and 3 for the
latter. For a given set of dielectric constant \( \epsilon \), a very precise
determination of \( D \) is obtained with a \( \pm 0.2 \text{ nm} \) error.
Actually the main uncertainty is due to the deviation of the
\( \epsilon \) values measured by different authors. For instance, very
similar fitting can be performed with the \( \epsilon \) data reported by
Palik,\textsuperscript{19} yielding \( D = 21 \) and 31 \text{ nm}. Including this systematic
error, the overall precision on the \( D \) value can be estimated
to be smaller than 1 \text{ nm}.
Femtosecond pump–probe experiments were performed on
these identified single nanoparticles using the same setup.
The two femtosecond near-infrared and blue beams were now
injected in the spatial modulation microscope. The individual
nanoparticle is excited by absorption of the femtosecond
near-infrared pulses (\( \lambda_{\text{np}} = 850 \text{ nm} \)). The induced transmis-
sion change \( \Delta T/T \) is probed close to the surface plasmon resonance with the frequency doubled part of the pulse train
at \( \lambda_{\text{np}} = 425 \text{ nm} \). The use of this same beam in spectral and
temporal measurements also permits precise alignment of
the setup and control of any evolution of the studied particle
through monitoring of its extinction spectrum. Both pump
and probe beams were tightly focused on the single nano-
particle with Gaussian spots of full width at half-maximum
570 and 290 \text{ nm}, respectively. The \( \Delta T/T \) signal was
monitored as a function of the pump–probe delay using a
classical pump–probe setup. It uses mechanical chopping of
the pump beam at 2 \text{ kHz} and lock-in detection of the
transmitted probe beam. Because of the excellent laser
stability, high sensitivity is achieved with a noise level in the
\( 10^{-6} \) range for \( \Delta T/T \) measurements.
When a single nanoparticle is illuminated by a beam
focused over an equivalent spot size, \( S_{\text{pp}} \) (top hat spatial profile of same energy), the sample transmission is given

\[ \sigma_{\text{ext}}(\lambda) = \frac{18\pi V \epsilon_m^2}{\lambda} \epsilon(\lambda) \left[ \epsilon(\lambda) + 2\epsilon_m^2 \right] \]
the electron kinetics it reflects. In these experiments, permits precise analysis of the Figure 2, inset, showing that two-photon absorption is maximum value is proportional to the pump excitation amplitude is consistent with the estimated one and its Figure 2 for three different pump powers. The excitation to typically 10^3 D measured in the energy of the surface plasmon resonance, the ultrafast nonlinear lattice coupling. In silver, for a probe pulse in the vicinity of the intrinsic electron scattering and cools down by electron-electron transfer time, \( \tau_{\text{e-ph}} \) of 950 fs at low excitation that strongly increases with pump power (Figure 3b). The low-energy \( \tau_{\text{e-ph}} \) values are consistent with the intrinsic electron–lattice energy transfer time, \( \tau_{\text{e-ph}} \) \approx 850 fs, measured in a large ensemble of matrix embedded D \approx 25 nm nanoparticles (about 10^5) in the weak electron perturbation regime.6

The dependence of the energy transfer time on the pump power and its different behavior in the 21 and 30 nm particles

by \( T \approx T_s(1 - \sigma_{\text{ex}}(\lambda_{\text{pk}})/S_{\text{pk}}) \) where \( T_s \) is the transmission when no particle is under the focal spot. The pump-induced transmission change can thus be written

\[
\Delta T/T \approx -(\Delta \sigma_{\text{ex}}/\sigma_{\text{ex}})(\sigma_{\text{ex}}/S_{\text{pk}})
\]

The first term is the relative modification of the extinction cross section induced by the pump pulse. It can be estimated from classical pump–probe experiments on nanoparticle ensembles. It depends on the amount of energy injected in the electron gas and varies from about 10^{-2} for strong excitation to typically 10^{-3}–10^{-4} in the low perturbation regime (see below). The second term, proportional to the linear extinction of one nanoparticle, is the overall time-domain signal reduction factor due to probing a single object. For silver nanoparticles in the 20–30 nm range, it is of the order of 10^{-2}, leading to a \( \Delta T/T \) signal in the 10^{-4}–10^{-6} range, detectable by our apparatus.

The time evolution of the transmission change \( \Delta T/T \) measured in the \( D = 30 \text{ nm} \) silver nanoparticle is shown Figure 2 for three different pump powers. The \( \Delta T/T \) amplitude is consistent with the estimated one and its maximum value is proportional to the pump excitation (Figure 2, inset), showing that two-photon absorption is negligible. The good signal over noise ratio of the data permits precise analysis of the \( \Delta T/T \) time behavior and thus the electron kinetics it reflects.1 In these experiments, absorption of an infrared pump pulse creates a strongly athermal conduction electron distribution that thermalizes by electron–electron scattering and cools down by electron–lattice coupling. In silver, for a probe pulse in the vicinity of the surface plasmon resonance, the ultrafast nonlinear response essentially reflects the time-dependent excess energy \( \Delta e_0 \) of the electron gas, as previously reported and modeled for ensemble measurements.20 Consequently, the \( \Delta T/T \) signal rise follows energy injection and is limited by the duration of the pulses. Its decay reflects the losses of the electron gas energy to the lattice that can thus be analyzed in a single particle.

For the different pump powers used here, almost exponential decays of \( \Delta T/T \) are observed (Figure 3). Even for the lower excitation, the decay is followed over more than 1 decade yielding a time constant \( \tau_{\text{e-ph}} \) \approx 900 fs for the \( D = 30 \text{ nm} \) particle (Figure 4). For higher pump energies, longer \( \Delta T/T \) decay times are observed with \( \tau_{\text{e-ph}} \approx 1.3 \text{ ps} \) for the largest energy. Similar results were obtained for the \( D = 21 \text{ nm} \) nanoparticle, with a comparable energy transfer time \( \tau_{\text{e-ph}} \) of 950 fs at low excitation that strongly increases with pump power (Figure 3b). The low-energy \( \tau_{\text{e-ph}} \) values are consistent with the intrinsic electron–lattice energy transfer time, \( \tau_{\text{e-ph}}^0 \approx 850 \text{ fs} \), measured in a large ensemble of matrix embedded \( D \approx 25 \text{ nm} \) nanoparticles (about 10^5) in the weak electron perturbation regime.6

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Nano Lett.
capacity is proportional to the electron temperature, \( C_e \) and the temperature rise induced by the pump pulse excitation can be characterized by the maximum electron temperature, \( T_{e max} \) (Figure 4). The above rate equation system can be analytically solved, yielding for moderate metal heating \( T_e, T_L \ll 100 T_0 \)

\[
\frac{T_{ext} - T_e(t)}{T_f} - \ln \left[ \frac{T_e(t) - T_f}{T_{exc} - T_f} \right] = \frac{G}{c_0 t_f} t
\]

where \( T_f \) is the final temperature of the thermalized electron–lattice system that, because of the large lattice heat capacity \( (C_L/C_e(T_0) \approx 100 \) in silver), is close to \( T_0 \). Though the predicted \( \Delta T_e \) decay is not exponential, \( T_e \) decay is not exponential, it can still be approximated by an exponential if \( \Delta T_{e max} \) does not exceed too much \( T_0 \). To compare the experimental and theoretical results, using eqs 4 and 5, we can define characteristic decay times \( T_e \) and \( u_e \), corresponding to the time for \( \Delta T_e \) and \( \Delta u_e \), respectively, to decay by 1/e (Figure 4).

This model can be generalized to metal nanoparticles down to a few nanometers in size for which quantum confinement effects weakly modify the electron properties. The key parameter in analyzing the observed electron energy kinetics is the excitation temperature \( T_{exc} \). This is difficult to precisely define in ensemble measurements, because of the pump beam intensity profile at the focal spot and of the fluctuations of the absorption cross section of the nanoparticles due to their size, shape, and environment dispersion. This can be done in a single nanoparticle provided that, as here, it is in situ optically characterized. The amount of energy absorbed by the studied particle \( u_{abs} \) can be estimated using the absorption cross section at the pump wavelength. As this is too weak in the near-infrared region to be directly measured, it is calculated from the extinction spectra measured around the surface plasmon resonance using its fitting by the Mie theory (Figure 1). Taking into account electron energy losses to the lattice during the duration of the pump pulse, the effective maximum heating for the \( D = 30 \) nm nanoparticle is estimated to be in the 110–430 K range (Figure 4b). It depends on the set of bulk \( c \) values, with the Johnson and Christy data yielding a larger electron temperature rise \( \Delta T_{e max} \) than the Palik data. This uncertainty is mostly responsible for the large error bars for the \( \Delta T_{e max} \) value (Figure 4b). For the \( D = 21 \) nm particle, excitation is larger for the same pump power, and \( \Delta T_{e max} \) is estimated to vary from 220 to 380 K. The decay times measured for a given electron temperature rise in the two studied particles are found to be in very good agreement with the predictions of the two temperature model.
for the $\Delta u_e$ kinetics (Figure 4b). This is consistent with the fact that for our probing conditions, the measured signal is proportional to $\Delta u_e$. The electron–phonon coupling constant, $G$ (or equivalently $r_{e-ph}^0$) measured in the bulk material has been used, confirming that it is weakly modified by size reduction for particles in the few tens of nanometer range.6

In conclusion, using a spatial modulation microscope coupled with a high sensitivity two-color femtosecond pump–probe setup, we have measured the ultrafast nonlinear response and the correlated electron kinetics of single small silver nanoparticles with sizes of 21 and 30 nm. The use of the same apparatus for spectral and temporal measurements permits in situ optical identification of the studied nanoparticle. The electron–phonon energy transfer times deduced from the single particle time response can thus be quantitatively compared and are found in good agreement with the predictions of the two temperature model. These results can thus be extended to smaller particles with the predictions of the two temperature model. These studies could be readily extended to smaller particles with diameter in the 10 nm range, for which size-dependent energy exchange kinetics has been demonstrated in ensemble measurements.5 This first femtosecond investigation of the transient absorption of a single metal nanoparticle opens up many possibilities for precise analysis of the ultrafast properties and electron kinetics of a metal nanoobject as a function of its size, shape, and environment.

Acknowledgment. The authors thank Conseil Régional d'Aquitaine for financial support.

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NL0524086