Optical detection and femtosecond spectroscopy of a single nanoparticle

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Received 24 May 2011
Accepted for publication 14 June 2011
Published 15 July 2011
Online at stacks.iop.org/ANSN/2/035011

Abstract
An extension to semiconductor quantum dots of the spatial-modulation technique, demonstrated for the optical detection and linear spectroscopy of a single metal nanoparticle, is described. The association of this approach to a high sensitivity femtosecond pump–probe setup is discussed and applied to the investigation of the acoustic vibration of a single silver nanoparticle.

Keywords: optical detection, femtosecond spectroscopy, single nanoparticle

Classification numbers: 2.02, 4.02

1. Introduction
Experimental investigation and modeling of the new properties of nanoobjects and nanomaterials has been an intense field of research during the last decade. This interest is motivated by the possibility of modifying these properties, playing with the size, geometry, structure and composition of a nanoobject. The main underlying fundamental mechanisms are electron and phonon quantum confinement, classical dielectric confinement effects (i.e. size reduction below a characteristic length, e.g. the wavelength for the optical response), an enhanced role of the interfaces, formation of new structures or nanoscale interaction between nano-entities.

Determination of the relative impact of these effects in different nano-objects is not only of major fundamental interest but also a necessary advance for fully exploiting nanosystems and developing new ones for applications.

In the optical domain, size reduction mostly translates into the apparition of morphological resonances, of different origins in semiconductor and metal nanoparticles. This is associated with quantum confinement in the former, and essentially due to the classical dielectric confinement (local field) in the metal case, leading to the well-known surface plasmon resonance [1–3]. In this context, femtosecond lasers and time-resolved optical techniques have emerged as powerful tools not only for the investigation of the nonlinear optical response of nanostructured materials but also for analyzing the interaction mechanisms of elementary excitations, e.g. free carriers, excitons and phonons [4, 5]. Furthermore, as compared with other experimental techniques, optical ones are non-contact, permitting the investigation of matrix embedded nanoobjects.

Up to now, most time-resolved optical investigations have been performed simultaneously with probing a large number of particles, typically 10⁴–10⁶. Due to the unavoidable dispersion of the size, geometry and environment of the particles, only a mean response is measured. This limitation has been circumvented using high quality samples with weak size and shape dispersions and by performing experiments in environment-independent conditions [6, 7]. However, such an approach cannot be used when strongly size- or shape-dependent effects or particles synthesized with limited geometry control are investigated. Experimental studies have then to be performed at the level of a single nano-object, which requires development of very high-sensitivity spectroscopic tools.

Time-domain investigation of the luminescence of a single nano-object is now a routine experiment but is limited to picoseconds time resolution and to highly luminescent objects. Reaching femtosecond resolution requires the use
of a pump–probe time-resolved technique, i.e. detection of the transient change of the absorption or scattering of a nano-object induced by a pump pulse. The first step in such an approach is to optically detect a single nanoparticle in situ. The near-field optical technique (SNOM) has been exploited to detect a single semiconductor or metallic nano-object and study its ultrafast response [8–10]. The complexity of these studies and of their interpretation due to tip-particle interaction in the case of metallic systems [11] has fostered the development of far-field techniques. Single metal nanoparticles were observed by detecting their light scattering [12], a method that has been extended to the femtosecond time domain in metallic nano-objects (80 nm gold nanospheres and nanorods [13, 14]). As the efficiency of light scattering by a particle decreases with the square of its volume \( V \) [1–3], these studies are limited to relatively large sizes. Absorption scaling as \( V \) strongly dominates over scattering for small particles and is then the parameter to monitor [15, 16]. Quantitative detection of the extinction, i.e. absorption for small particles, of a single metal particle has been demonstrated using a spatial-modulation spectroscopy (SMS) technique [17, 18], and extended to femtosecond pump–probe optical measurements of a metal nanosphere down to 20 nm [15]. An extinction change geometry is used with the additional and key advantage of permitting optical characterization of the nanoparticle via its linear extinction spectrum. In this paper, we discuss some results obtained on a single metal nanoparticle using the SMS technique combined with a femtosecond pump–probe setup, and its possible extension to the investigation of single semiconductor quantum dots.

2. Single nanoparticle detection: spatial modulation spectroscopy

The first step in the time-resolved pump–probe investigation of a single nanoparticle is its in-situ optical detection. This is done using the SMS technique, which is based on periodically modulating the position of a nanoparticle in the focal spot of a laser beam focused close to the diffraction limit (figure 1). Assuming that the particle is much smaller than the focal spot diameter, the transmitted power \( P_t \) is given by

\[
P_t = P_i - \sigma_{ext}(\lambda) I(x, y),
\]

where \( P_i \) is the incident light power and \( I(x, y) \) its intensity at the position \((x, y)\) of the particle in the focal plane. Modulating this position in this plane results in a modulation of \( P_t \). A signal proportional to the first or second derivatives of \( I(x, y) \) is obtained when demodulating \( P_t \) at the fundamental or second harmonic of the modulation frequency \( f \), respectively. In both cases, the measured modulated amplitude of \( P_t \) yields the absolute value of the extinction cross-section, \( \sigma_{ext}(\lambda) = \sigma_{abs}(\lambda) + \sigma_{sc}(\lambda) \) of the particle under study with a sensitivity in the few \( \text{nm}^2 \) range [13]. Scanning the sample position with the \( x,y \) scanner (figure 1), two-dimensional images of the sample surface can be recorded, permitting localization of the different nanoparticles. The spatial resolution is about half the optical wavelength, requiring the use of diluted samples, ensuring that only one particle is under the focal spot. The sample is prepared by spin-coating a colloidal solution of nanoparticles on a glass substrate. Properly choosing the deposition conditions, samples with the required surface density of less than one particle per \( \mu \text{m}^2 \) were prepared.

Figure 1. Schematic of the combined spatial modulation spectroscopy (SMS) and time-resolved pump–probe setup for investigating a single nanoparticle. The transmission microscope was formed by a focusing 100× microscope objective, a piezo-electric element modulating the sample position at frequency \( f \) along the \( y \) direction, the \( x,y \) scanner, a collecting \( x \) 100 objective, a photodiode (PD), a digital voltmeter (DVM), and a lock-in amplifier demodulating the signal at \( f \) or \( 2f \). SMS measurements were performed using either the fundamental beam of a tunable Ti:sapphire femtosecond oscillator or its second harmonic created in a \( \text{BaB}_2\text{O}_4 \) (BBO) crystal. A supercontinuum light source generated in a photonic crystal fiber (not shown) was also used. Time-resolved measurements were performed, sending both the fundamental and the frequency doubled pulses into the setup. In the case of a silver nanosphere, the latter was the probe pulse and was frequency selected after the sample by a color filter (CF). The former was the pump beam and was modulated by a mechanical chopper (Ch) to perform lock-in detection of the probe pulse transmission change.
This experimental method is particularly well suited to the detection of a non-luminescent nanoparticle, such as a metallic one. It has been demonstrated in this context and exploited to quantitatively analyze the linear optical response of different metal nanoparticles as a function of their size and shape. This is illustrated in figure 2 in the case of individual silver nanoparticles prepared from a colloidal solution of particles with a mean diameter of about 10 nm. Measurements were performed around the surface plasmon resonance frequency of the silver particles using the second harmonic of a Ti:sapphire femtosecond laser as the light source (figure 1). The part of the transmitted light modulated at \( f \) was detected, each single nanoparticle showing up as two main peaks (figure 2). The amplitude of the measured \( x-y \) profile was determined by the extinction cross-section of the particle, i.e. by its absorption cross-section, \( \sigma_{abs}(\lambda) \), for small noble metal particles (smaller than about 30 nm). The latter being proportional to the particle volume [1–3], the nanoparticle characteristics (size and anisotropy) can be deduced through quantitative measurement of the \( \sigma_{abs} \) spectrum and comparison with a theoretical model (figure 2) [17, 18].

We have extended this method to semiconductor nanoparticles (CdSe). Using the same approach, the sample was prepared by spin coating a colloidal solution with a mean nanoparticle diameter of 40 nm. As in the metal case, the semiconductor particles showed up as changes in the relative power transmitted by the sample when a wavelength smaller than the exciton one was used (figure 3). This permitted their detection, opening the way to their first quantitative absorption spectroscopy. However, for the experimental setup used here, a decrease in the signal amplitude was observed with time when leaving the nanoparticle under the focal spot. This indicates degradation of the nanoparticle by the optical beam (the mean incident power is about 1 \( \mu \)W, with a repetition rate of 8 MHz and a focal spot...
3. Femtosecond spectroscopy of a single nanoparticle

Optical detection of a single metal nanoparticle and its characterization through its linear extinction signature opens up many possibilities for the nonlinear spectroscopy of a single nano-object. In this context, the extension of time-resolved femtosecond nonlinear spectroscopy to a single nanoparticle is particularly interesting [15]. Similarly to ensemble measurements, this opens the way to the investigation of the physical origin of its nonlinear optical response, and its electronic and vibrational kinetics [5]. In this context, we have recently shown that combining the SMS technique with a high sensitivity femtosecond pump–probe setup (figure 1), the nonlinear study of a single silver nanosphere with femtosecond resolution can be performed for sizes down to 20 nm [15]. This was optically determined from the single-particle absorption spectrum, time-resolved transient absorption measurements then being performed with the same setup (figure 1), yielding precise information about the particle electron–lattice coupling. In this type of experiment, the transient change in the probe transmission $\Delta T(\lambda_{\text{probe}})$ induced by optical excitation of a single nanoparticle by the pump pulse is monitored. This is directly proportional to the transient modification of the nanoparticle extinction cross-section $\Delta \sigma_{\text{ext}}(\lambda_{\text{probe}}, t_{\text{D}})$ permitting its measurement. As in metal films, the measured transient response can thus be connected to the optically induced change of the metal dielectric function, i.e. to the third order nonlinearity of the material [5].

Using this same femtosecond approach, the vibrational acoustic response of a single metal nanoparticle can be investigated, monitoring $\Delta \sigma_{\text{ext}}(\lambda_{\text{probe}}, t_{\text{D}})$ on a longer-picosecond-time scale. Such a measurement is shown in figure 4 in the case of silver nanospheres. The signal rise and short-time decay ($t_{\text{D}} \lesssim 3 \text{ ps}$) are dominated by the transient electronic response, i.e. heating of the electrons by the pump pulse and their subsequent cooling by energy transfer to the lattice. As previously discussed [15], the latter permits measurement of the electron–lattice energy transfer time, about 850 fs here. On a longer time-scale the signal shows oscillations with a period of about 7 ps. As in ensemble measurements using a similar pump-probe technique, these can be ascribed to acoustic vibration of the nanoparticle launched by fast transfer to the lattice of the energy injected by the pump pulse in the conduction electrons [19–21].

This preferentially launches the isotropic modes of the particle, with a dominant response of the fundamental breathing mode, as observed here [19–21]. Using the elastic model theory and assuming a spherical particle, the measured period corresponds to a particle diameter $D_{\text{acoustic}}$ of about 23 nm. This value is consistent with that estimated from quantitative measurement of the extinction cross-section of the nanoparticle using the SMS technique, $D_{\text{opt}} \approx 21 \text{ nm}$. These first results open the way to correlation of the optical and acoustical responses of a single nano-object.

4. Conclusion

Optical detection and spectroscopy of a single metal nanoparticle with the spatial modulation technique, first demonstrated on single metal nanoparticles, can be straightforwardly extended to the quantitative investigation of a semiconductor quantum dot, and more generally any absorbing single object. This detection of a single quantum dot constitutes the first step towards its femtosecond investigation. This can be performed by associating the spatial modulation technique with a femtosecond pump–probe setup, opening up many perspectives for the analysis of the fundamental properties of a single nanoparticle. In particular, this approach can be used to monitor both the electron–lattice energy exchange kinetics and the acoustic vibration of a single particle, and thus to precisely correlate their dependence on the size, shape and environment of the particle.
Acknowledgment

The authors are grateful for financial support from the CNRS—VAST program. NDF also acknowledges support from Institut Universitaire de France.

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