

Nano ultrasonic measurements of nanoparticles

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Abstract. Metallic nanoparticles have been widely used for the last two decades as their optical properties can be exploited in fields such as physics, medicine and biology. The scattering and absorption properties of these devices are dependent on the material, the surrounding media and the size. The latter is crucial for many applications and a reliable measurement is a must. However, the current applications have some limitations such as they are destructive, cannot provide the size of individual particles or they use high vacuums. In this paper, we propose the use of an optical microscope which allows the measurement of multiple metallic nanoparticles non-destructively providing the size of each single particle.

INTRODUCTION

The physical and optical properties of metallic nanoparticles have been heavily studied in the last few decades. This interest stems from their specific behaviour that depends on the particle size and shape and is very different from that of the bulk material; therefore, characterising their sizes is an essential step to understand their properties.

There are several techniques which can provide size information of metallic nanostructures such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM) or dynamic light scattering (DLS). However, they can affect the nanoparticle in a destructive way, can only provide information of either individual particles or low concentrations. For example, the use of high vacuums in TEM and SEM does not allow the sample to be in a liquid medium, the mechanical probe used by AFM is in contact with the particle which might affect its shape, and DLS cannot provide information of single particles.

In this paper, we propose the use of an optical technique, time-resolved pump-probe spectroscopy [1, 2, 3, 4, 5], to characterise non-destructively the size of metallic nanoparticles where information from individual or groups of particles can be obtained with very high resolution.

In this scheme, metallic nanoparticles can work as sources of ultrasound when a short optical pulse (pump laser) is used to thermally excite them producing GHz acoustic waves [6]. The vibrational response of a nanoparticle can be detected in the time domain by measuring the changes in the scattered light. To access the very high frequency range of the vibrations of these small particles, the scattering is detected using pulsed lasers in a pump-probe configuration [7, 8]. Both, the generation and detection processes, can be enhanced by matching the pump and probe wavelengths with the optical resonances of these nanoparticles.

Mechanical response

The vibrational frequency is a function of the material properties, the particle size and, to a lesser extent, the surrounding media. This can be described in terms of vibrations of a homogeneous elastic body embedded in an infinite

homogeneous medium [9]. This macroscopic model is valid for particles with diameter larger than a few nanometres where continuum mechanics and bulk elastic constants can be used [10]. The complex radial frequency modes, $\omega_n(R) = \xi_n v_L^{(s)}/R$, depend on $v_L^{(s)}$, the longitudinal sound velocity of the particle; R , the radius; and ξ_n , the eigenvalues, given by Equation 1.

$$\xi_n \cot(\xi_n) = 1 - \frac{\xi_n^2(1 + i\xi_n/\alpha)/\eta}{\xi_n^2 - 4\alpha^2\gamma^2(1 - 1/\eta\beta^2)(1 + i\xi_n/\alpha)} \quad (1)$$

where the parameters are defined by:

$$\begin{aligned} \alpha &= v_L^{(m)}/v_L^{(s)}, \\ \beta &= v_T^{(m)}/v_T^{(s)}, \\ \gamma &= v_T^{(m)}/v_L^{(m)}, \\ \eta &= \rho^{(m)}/\rho^{(s)}. \end{aligned}$$

where $\rho^{(m),(s)}$ and $v_{L,T}^{(m),(s)}$ are the density and longitudinal (L) or transverse (T) sound velocity of the medium (m) and sphere (s).

It is assumed a weak coupling between the sphere and the medium ($Im(\xi_n) \ll Re(\xi_n)$) and weak damping []. Therefore, the radial mode frequencies, ω_n , can be related to the real part of ξ_n ($Re(\xi_n) \approx (n+1)\pi$) and the damping of the sphere modes, γ_n , is proportional to the imaginary part of ξ_n ($Im(\xi_n) \approx \eta\alpha$). Hence, the main breathing mode frequency ($n=0$) of a nanoparticle and the damping between it and the media are expressed in equation 2 and 3, respectively.

$$f_n = Re(\xi_n) \frac{v_L^{(s)}}{2\pi R} \approx (n+1) \frac{v_L^{(s)}}{2R} \quad (2)$$

$$\gamma_n = Im(\xi_n) \frac{v_L^{(s)}}{R} \approx \frac{\rho^{(m)}}{\rho^{(s)}} \frac{v_L^{(m)}}{R} \quad (3)$$

INSTRUMENTATION

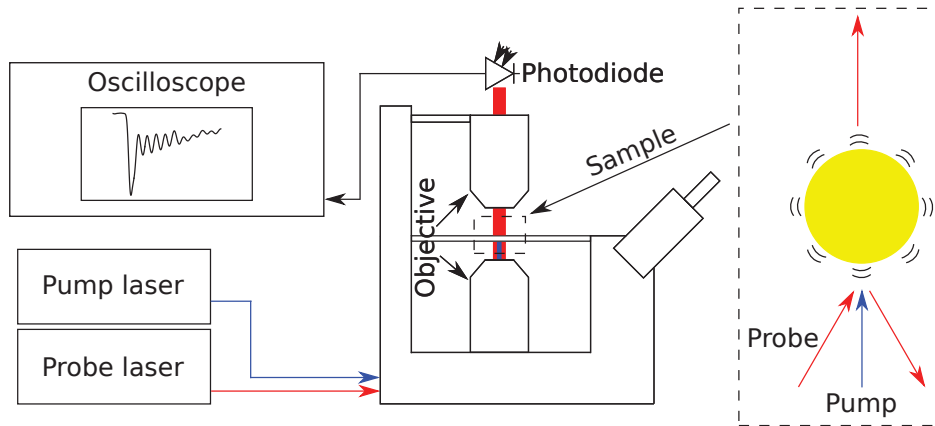


FIGURE 1. Schematic of the time-resolved pump-probe spectroscopy system and the experiment from the nanoparticles point of view.

The imaging experiment was conducted using a custom microscope built around an Olympus IX73 inverted microscope body (figure 1). This was arranged in a conventional inverted microscope layout with an additional object lens on top, similar to a 4π microscope layout. With this arrangement it was possible to pump, probe and image the

nanoparticles from one or both sides of the sample simultaneously. In addition to conventional imaging optics the system allowed two laser beams to be focused into the sample. These beams were provided by a dual Ti:Sapphire (Tsunami, Spectra-Physics) laser asynchronous optical sampling (ASOPS)[7, 8] and produces ~ 100 fs pulses with an 80 MHz repetition rate. The ASOPS electronics allow the timing of the laser pulse from each laser to be precisely controlled and for the time delay between the pulses to be swept from 0-12.5 ns every 100 μ s (10 kHz). While the lasers were wavelength tunable, these experiments were performed with fixed wavelengths of 420 and 780 nm for the pump and probe beams, respectively. They were brought to the sample focused an Olympus LUC PLFLN x20 objective (0.45 NA).

Maximum average power of 1 mW pump and 2 mW probe (measured at sample) were used, corresponding to pulse energies of 10 pJ and 25 pJ and peak powers of 100 W and 250 W, respectively. The sample was scanned by moving electromechanical stages (Thorlabs MLS 203-1) with a minimum step motion of 100 nm. The probe beam was detected using a Thorlabs PDA36A which effectively low pass filters the optical signal removing the individual pulses. The signal was then collected by a Lecroy HRO66Zi oscilloscope. With this arrangement optical frequencies detected were down shifted by a factor of 8000 with the 0-100 GHz frequencies being converted to 0-12.5 MHz. The oscilloscope performed high speed averaging of this signal and, typically, 30,000 averages per point are taken during scanning which takes around 9 s to acquire.

RESULTS

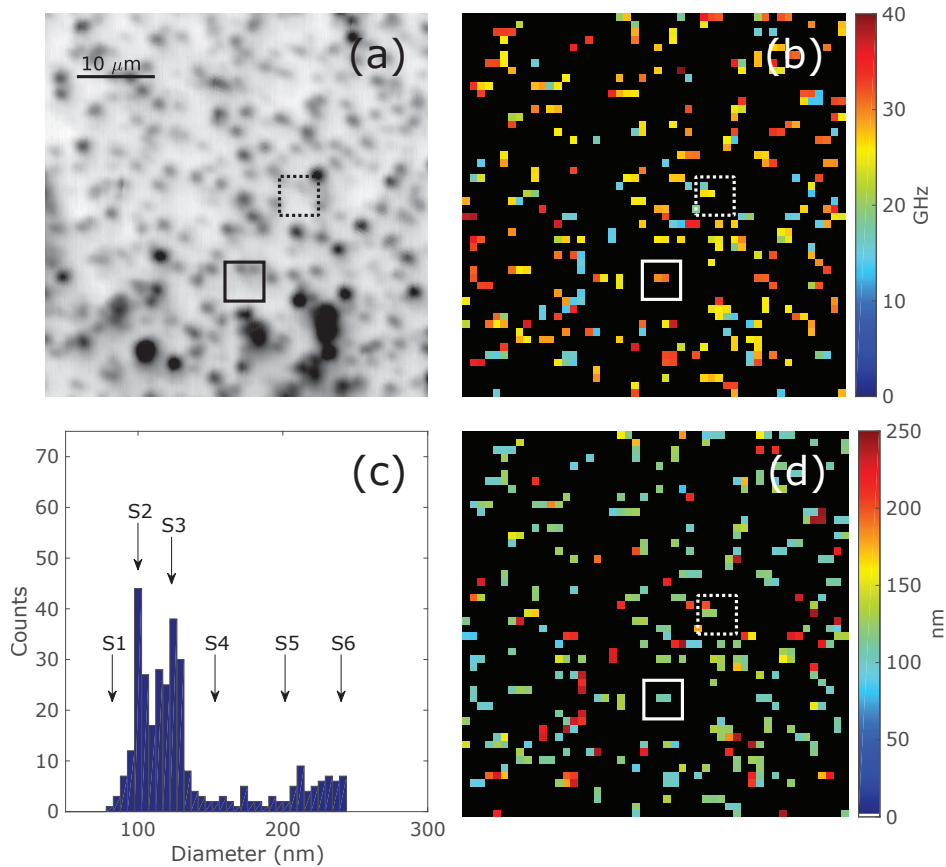


FIGURE 2. Area scan of multiple metallic nanoparticles measured by time-resolved pump-probe spectroscopy. (a) is the optical picture, (b) is the acoustic data, (c) is a histogram of the size distribution, and (d) is the real size calculated by the acoustic data.

The size characterisation of metallic nanoparticles was investigated using six different sizes of gold nanoparticles: 80, 100, 125, 150, 200 and 250 nm (samples S1-S6, respectively) in an air surrounding medium. Their theoretical breathing mode frequencies obtained by equation 2 (where v_L is 3240 m/s) are 40.5, 32.4, 25.9, 21.6, 16.2 and 12.9 GHz, respectively. However, this will vary depending on the actual size of the particle, allowing size characterisation.

Figure 2 shows the experimental data taken with our optical microscope from a sample containing a random mixture of gold nanoparticles with different sizes (samples S1-S6). The sample is scanned over an area of $50 \times 50 \mu\text{m}^2$ with a step-size of $1 \mu\text{m}$. This is the same size as the spot of the pump laser, which means, all the particles in the scanned area are excited.

An optical picture is shown in figure 2a where different apparent particle sizes can be seen. After signal processing, the breathing mode frequency for each particle is obtained, as shown in figure 2b. Each frequency can be related to the actual size of the particle (Equation 2) giving a study of the population of sizes (Figure 2c) or an ultrasonic picture in nm (Figure 2d).

As it can be seen in figure 2, the optical and acoustic data do not match. Where the optical picture shows individual particles, the acoustic data shows several frequencies which suggests group of particles. This shows that measuring the vibrational frequency using time-resolved pump-probe spectroscopy allows the size characterisation of groups of particles more accurately than using their optical response.

This technique also allows the characterisation of individual particles by scanning specific areas with finer step-size. This is shown in figure 3 where two regions were selected from figure 2 marked as solid and dashed square areas. These scanned areas are $5 \times 5 \mu\text{m}^2$ with 100 nm step-size. Both optical pictures show a single dip in intensity and shape (Figure 3a and 3c); however, the ultrasonic pictures given by our microscope are slightly different. Figure 3b shows a frequency of 25.39 GHz, whereas a frequency of 30 GHz can be seen in figure 3d suggesting that the first particle is larger than the second one. The actual size of these particles are 128 and 108 nm, respectively.

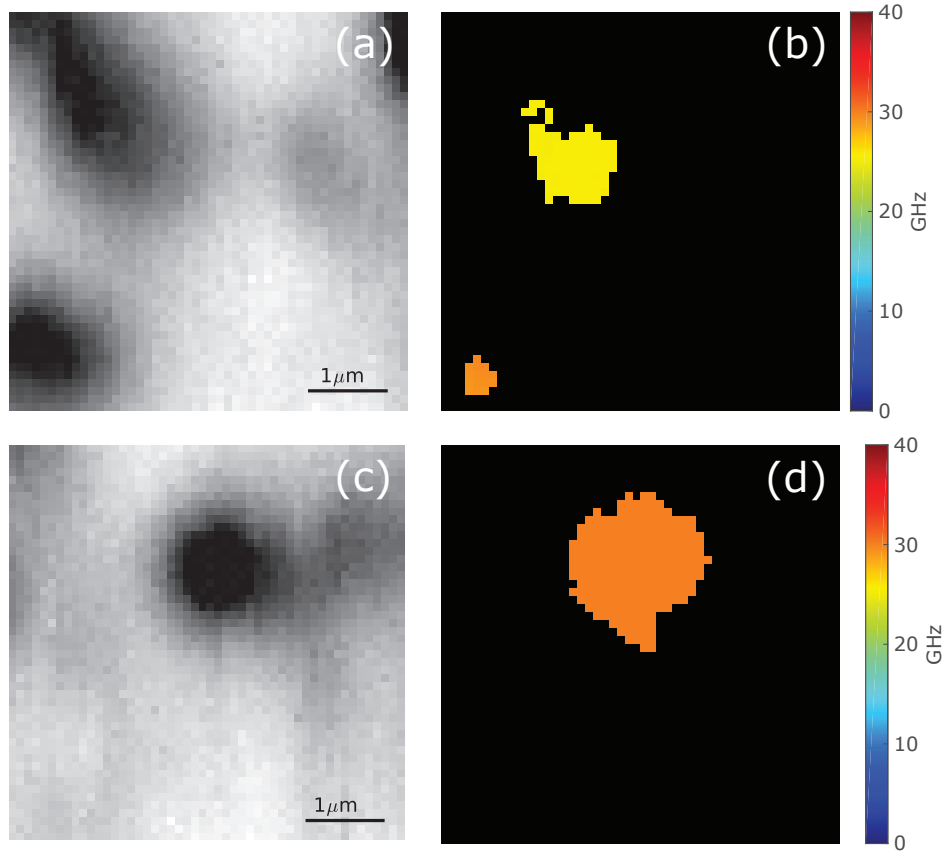


FIGURE 3. Area scan of individual metallic nanoparticles measured by time-resolved pump-probe spectroscopy. (a,c) are the optical picture, (b,d) are the acoustic data.

CONCLUSIONS

By using time-resolved pump-probe spectroscopy which allows to access the GHz vibrational frequencies of metallic nanoparticles, we have been able to characterise their sizes in a non-destructively way.

As we have prior knowledge about the material properties of the particles and the surrounding medium, the measured vibrational frequencies can be directly related to the particle sizes. This allows us to obtain information of multiple and individual particles very accurately, including a study about the size polydispersity.

This optical technique might allow high-resolution detection of several nanoparticles inside the point spread function based on their vibrational mode frequencies and their localisation if we centroid the amplitude maps at each particle frequency.

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