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Thermo-optical properties of gold nanoparticles in colloidal systems

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Abstract

In this work, we report the thermo-optical properties of nanoparticles in colloidal suspensions. Spherical gold nanoparticles obtained by laser ablation in condensed media were characterized using thermal lens spectroscopy pumping at 532 nm with a 10 ns pulse laser-Nd-YAG system. The obtained nanoparticles were stabilized in the time by surfactants (sodium dodecyl sulfate or SDS) in water with different molar concentrations. The morphology and size of the gold nanoparticles were determined by transmission electron microscopy (TEM) and UV–visible techniques. The plasmonic resonance bands in gold nanoparticles are responsible for the light optical absorption, and the positions of the absorption maximum and bandwidth in the UV–visible spectra are given by the morphological characteristics of these systems. The thermo-optical constants such as thermal diffusion, thermal diffusivity, and (dn/dT) are functions of the nanoparticle sizes and the dielectric function of the media. For these reasons, the thermal lens (TL) signal is also dependent on nanoparticle sizes. An analysis of the TL signal of the nanoparticles reveals the existence of an inverse dependence between the thermo-optical functions and the size. This methodology can be used in order to evaluate these systems and characterize nanoparticles in different media. These results are expected to have an impact in bioimaging, biosensors, and other technological applications such as cooling systems.

Keywords: nanoparticles, thermo-optical properties, colloidal systems

1. Introduction

The special interest in the thermal properties of colloidal nanoparticles has been driven by their wide range of applications. The colloidal suspensions formed with nanoparticles and organic solvents can be used as antibacterial medical treatments [1, 2], photo-thermal therapy [3], and cooling systems [4] among others. These systems must be characterized in terms of particle morphology, size distribution, and colloidal stability using techniques such as absorption spectroscopy, transmission electronic microscopy (TEM), and atomic force microscopy (AFM). However, in order to determine the thermal properties of the nanofluids, thermo-optical techniques are required. It is not possible, in general, to carry out a straightforward relationship between thermo-optical function and morphological characteristics of these systems. Thermal lensing is widely used to determine the thermo-optical coefficients of different materials (gas, liquids, or solids). In a typical pump–probe mode-mismatched thermal lens (TL) experiment, the pump beam is used to generate the temperature distribution in the sample, due to the fact that the sample has both linear and nonlinear absorption at the pump beam wavelength; distortions in the probe beam wavefront at the far field are induced. These distortions are used to calculate the TL signal (TLS) as a function of the intensity of the pump beam by using the Fresnel diffraction approximation. For a nonlinear optical material that has linear and nonlinear absorption coefficients at the wavelength of the pump beam, according to the basic TPA process the beam intensity changes

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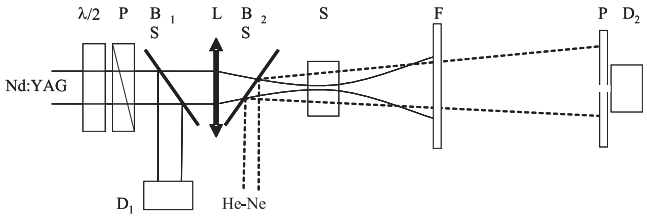

Figure 1. Thermal lens experimental setup.

along the propagation direction z-axis. We can calculate the TLS, which is defined as the relative change of the transmission through the small aperture for the carrier wave (CW) laser TL technique, and it is viewed as the degree of mode-mismatching of the probe beam and excitation beam in the sample at $z = 0$ [5]:

$$\mathrm{TLS}(0) = G\frac{8DA}{\kappa\lambda_\mathrm{p}}\left(\frac{\mathrm{d}n}{\mathrm{d}T}\right)E. \tag{1}$$

In this equation G is an experimental geometric factor given by

$$G = \frac{(e^2-1)w_\mathrm{p}^2 z_1 z_c}{e^2(4w_0^2 w_\mathrm{p}^2 z_c^2 + 4w_\mathrm{p}^4 z_c^2 + w_0^4(z_1^2+z_c^2))} \tag{2}$$

where A is the absorbance of the sample, z is the spatial coordinate. w_0 corresponds to the waist beam, $w_\mathrm{p} = w_0(2\ln 2)^{1/2}$, E is the energy of the pulse. κ is the thermal conductivity, D corresponds to the thermal diffusivity, $\mathrm{d}n/\mathrm{d}T$ is the thermo-optic coefficient of the sample, λ_p is the wavelength of the probe beam and z_1 is the distance between the sample and aperture plane. The Rayleigh range ($\pi w_\mathrm{p}^2/\lambda_\mathrm{p}$) and the radius at the sample position of the probe beam are respectively denoted by z_c and w_p. We assume that the heat generation in the liquid phase is instantaneous. This assumption is justified due to the duration time of the laser pulse (τ), which is in the nanosecond scale range, which is much less than the characteristic relaxation time associated with the photo-thermal effect ($t_\mathrm{c} = w_0^2/4D$), that is in the millisecond scale range. The rise in temperature of the medium is accompanied by a change in its refractive index ($\Delta n = (\mathrm{d}n/\mathrm{d}T)\Delta T$), which alters the propagation of the probe beam. From equation (1) it is possible evaluate the dependence between TLS and E in an experiment called I-scan [5, 6]. The data provided in this experiment can be linearly fitted in order to obtain the slope, ζ defined by:

$$\zeta = G\frac{8DA}{\kappa\lambda_\mathrm{p}}\left(\frac{\mathrm{d}n}{\mathrm{d}T}\right). \tag{3}$$

The values of ζ represent the global functional dependence between the thermo-optical parameters and the characteristics of colloidal nanoparticles. The contributions of each parameter on its own are very difficult to obtain because these quantities are related to each other.

2. Experimental details

The I-scan experimental setup is shown schematically in figure 1. The experiments were performed with a Q-switched mode locked Nd:YAG laser (Continuum Surelite) delivering 10 ns pulses at $\lambda_\mathrm{p} = 532$ nm with a repetition rate of 10 Hz. A half-wave plate ($\lambda/2$) placed before a Glan polarizer (P), allows the adjustment of the pump laser energy. Control of the input pulse energy is achieved by means of a beam splitter (BS1) sending about 4% of the total beam on a photodiode (D1) connected to a two-channel digital oscilloscope. Using a positive lens (L) the beam is then focused to a spot of radius $w_0 = 200$ μm at the focal plane, corresponding to a Rayleigh length $z_0 = 23.6$ cm in the air. The probe beam is the light from a 1 mW CW He–Ne laser ($\lambda = 633$ nm) and it passes through the sample (S), which is fixed at the waist of the excitation beam ($z = 0$). The samples consist in gold nanoparticles suspended in sodium dodecyl sulfate (SDS), which has a concentration of surfactant between 10^{-5} and 10^{-3} M, contained in quartz cells of 1 cm path-lengths. A second beam splitter (BS2) directs the probe light onto the sample in the coaxial direction of the pump beam. The interference filter (F) cancels the pump light behind the sample-cell. The probe beam finally propagates into the detection system consisting of a small aperture (1 mm), the photodiode (D2), and the digital oscilloscope. The absorption of the plasmonic resonance band [7] is detected using an Ocean Optics S2000 spectrometer.

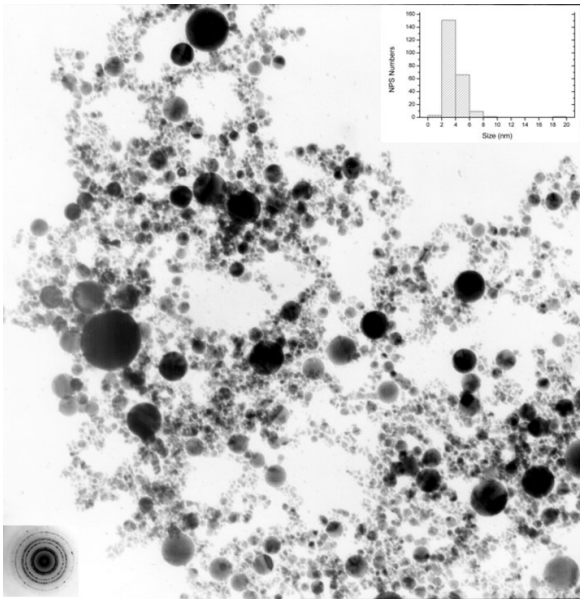

Figure 2. TEM micrographs and histogram of the spherical gold nanoparticles produced by laser ablation of a solid gold target immersed in SDS solution.

The samples were obtained by laser ablation of a gold plate in an aqueous solution in sodium dodecyl sulfate [8]. The size-control was obtained by proper tuning of the surfactant concentration, the laser fluence and numbers of shot [9–11]. The size and morphology of the gold nanoparticles were evaluated by transmission electron microscopy (TEM) using a JEOL JEM-550 TEM (figure 2). The samples for TEM investigation were prepared by placing a drop of colloidal gold solution on colodion coated copper grids and evaporating it in air at room temperature.

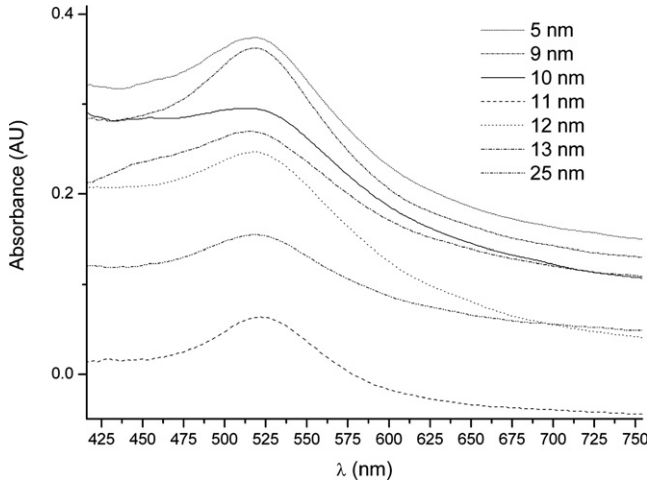

Figure 3. Absorptions spectra of spherical gold nanoparticles in colloidal suspensions.

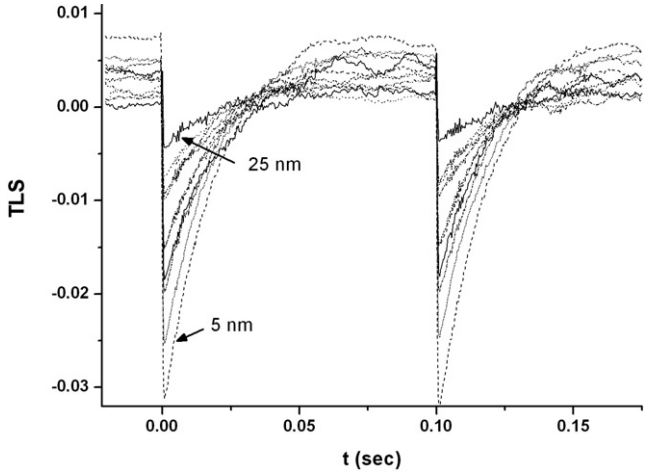

Figure 5. Thermal lens signal of gold nanoparticles with energy of 40 μJ pulse^{-1}.

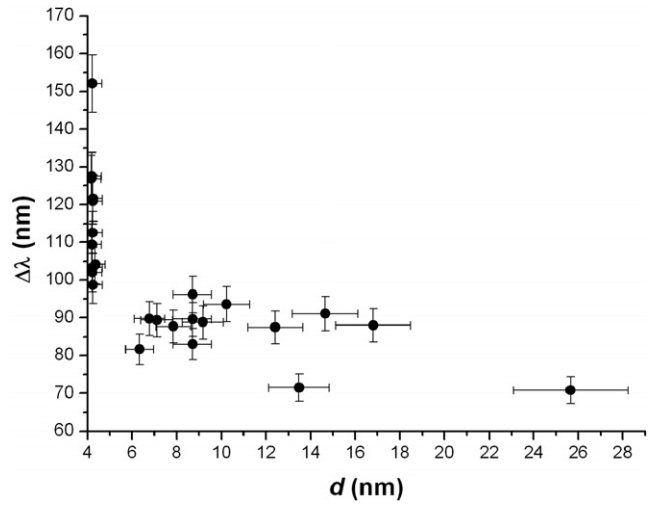

Figure 4. Size effects on the surface plasmon absorption bandwidth ($\Delta\lambda$).

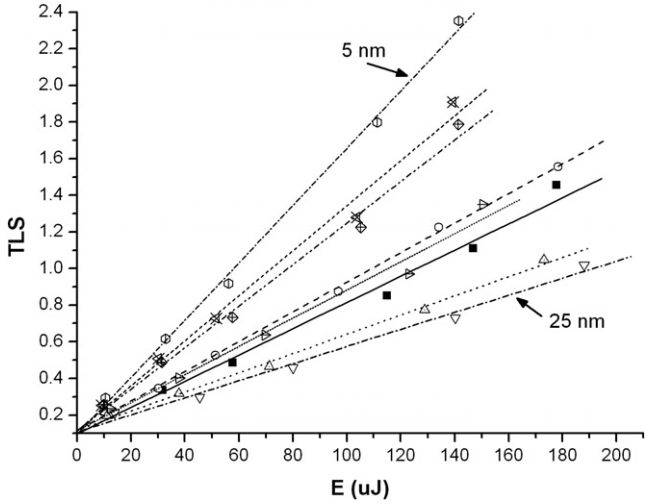

Figure 6. Variation of TLS with pump laser energy (I-scan) for gold nanoparticles with different mean sizes.

3. Results and discussion

Figure 3 shows absorbance spectra as a result of plasmonic resonance of different size gold nanoparticles in aqueous solutions. The shape of the bands suggests that the nanoparticles obtained are spherical, as can be observed in the TEM micrographs. The maximum of the absorption band is observed around 520 nm for all curves. The small displacement in the maximum position is attributed to nanoparticles size variations. The size dependence of the plasmon absorption is a consequence of the size-dependent dielectric function of the material.

The size effects on the surface plasmon absorption bandwidth ($\Delta\lambda$) are shown in figure 4. Experimentally, it is observed that the absorption bandwidth is inversely proportional to the nanoparticle size for shorter nanoparticles (<25 nm). This result has been reported in previous experimental works [12]. A quantum mechanical model developed recently also predicts this behavior [13]. For small nanoparticles, one gets responses associated with electron-surface scattering; due to the fact that the mean free path of the conduction electrons is limited because of the nanoparticle boundaries. This behavior vanishes as the sizes of the nanoparticles increase.

The temporal evolution of the TLS is presented in figure 5 for different nanoparticle sizes (5–25 nm). Analyzing the signal amplitude for different samples, we observed that TLS decreases with the increase of the mean nanoparticle size. We can neglect any thermal lens effect induced by the pump beam on the surfactant or the solvent, because these do not have light absorption at the pump beam wavelength. The results of the I-scan experiment performed with the same nanoparticle suspensions verified this behavior when TLS is studied as a function of the pump beam laser energy (see figure 6). The data from each sample can be linearly fitted as predicted by equations (1). These results suggest that the thermo-optical parameters are inversely proportional to nanoparticle size, ($\zeta(d) \propto 1/d$).

Suspensions of colloidal gold nanoparticles can produce a change in heat flux in liquids. Interaction between radiation and these systems is determined by its size and morphology. This dependence produces changes in thermo-optical parameters such as thermal conductivity and thermal diffusivity. In addition, high energy laser radiation can induce fragmentation [14], changing the properties of heat transfer in nanofluids. The I-scan experiment is an interesting alternative for the measurement of thermo-optical properties with high sensitivity, and such experiments are underway in our laboratory.

4. Conclusions

We have described a new approach based on the TL and I-scan techniques for the determination of thermo-optical properties of colloidal nanoparticle systems. Using this method, we have performed a comparison for different nanometer-size gold nanoparticles. These results show that thermo-optical function changes significantly with the size of the gold nanoparticles in the colloidal liquids systems. An increase of the thermo-optical parameters with the decrease of the mean size of the nanoparticles can be hoped for. In order to change the thermal properties of liquids we propose to use high energy laser radiation, because it can induce fragmentation in the nanoparticle system, modifying properties such as the heat transfer in nanofluids. These kinds of systems have therefore been suggested as potential 'intelligent coolants'. As illustrated in the present work, a specific dependence of each thermo-optical parameter alone is not possible, but these preliminary results are encouraging and show that a thermo-optical function must be proportional to $1/d$ for smaller nanoparticles. Work along these lines is currently in progress.

Acknowledgments

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