Photopyroelectric Techniques for thermo-optical characterization of gold nano-particles

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Abstract. Since the first methodology, proposed by Turkevich, to produce gold nanoparticles (AuNPs), improvements have been made as to allow better controllability in their size and shape. These two parameters play important role for application of gold nanoparticles since they determine their optical and thermal properties. Two photopyroelectric techniques for the measurement of the thermal diffusivity and the optical absorption coefficient for nano-particles are introduced. These thermo-physical properties were measured for the colloidal systems at different nano-particle´s sizes and, for optical properties, at three different wavelengths (405 nm, 488 nm and 532 nm). No significant difference, on thermal properties, was found in the range of nano-particles` sizes studied in this work; in opposition optical properties shown more sensitive to this parameter.

1. Introduction

Metallic nano-particles have shown potential applications especially in biomedicine (photothermal therapy and radiofrequency hyperthermia) due mainly to their optical properties, which can be conveniently changed by changing its size and morphology. At this respect gold nano-particles are very important since gold is a noble metal, not toxic for human been [1]. Simple and precise experimental techniques for optical and thermal characterization of nanofluids are then relevant since these two physical properties are important factors for such applications. In this work two photothermal techniques, for thermal diffusivity and optical absorption coefficient measurements for liquids, are used for thermal and optical characterization of gold nano-particles. Gold-nanofluids at different sizes, ranging between 5 to 60 nm in diameter, were used for this goal. The optical absorption coefficient at three different wavelengths (405 nm, 488 nm and 532 nm) was obtained and it was shown the strong dependence of this optical parameter on the nanoparticle´s size.

2. Theoretical bases

The mathematical model of the photopyroelectric methodologies for thermal and optical characterization of liquids involves the heat diffusion problem through a three layer system [2,3].

The heat source, for each case, consists of modulated radiation at fix modulation frequency, *f*, which, for the case of thermal diffusivity measurements [2], is absorbed on the surface of a strong absorbing material (Fig. 1) and, for the case of optical absorption coefficient measurements [3], is absorbed through the liquid sample under study (Fig. 2) by following the Beer-Lambert´s model for light absorption, with optical absorption coefficient *β*. The heat generated on each case travels through the liquid sample under study to reach the pyroelectric sensor which generates, on response, a voltage which is measured by means of a lockin amplifier.

The voltage difference on the pyroelectric sensor can be written as a complex expression that depends on the thermal and optical properties of the involved media and on the modulation frequency and thickness of the liquid sample as well.

However, if the modulation frequency is keep constant and the sample´s thickness, *L*, is taken as the only variable it can be shown that, under the appropriate experimental conditions, this voltage difference, $V(L)$, for the case of thermal diffusivity measurements, can be written in the very simple form $V(L)=C\exp(-\sigma L)$, where $\sigma=(1+i)(\pi f/\alpha)^{1/2}$; meanwhile that for the case of optical absorption coefficient measurements it can be written as $V(L)=D\exp(-\beta L)$. *C* and *D* are complex expressions which are independent on the sample´s thickness. The photopyroelectric phase in this last case is constant and this fact can be used as an experimental criterion as to validate the optical parameter to be measured.

The experimental procedure to obtain thermal diffusivity involves plotting the pyroelectric´s signal phase, as a function of the sample´s thickness, and carried out a linear fitting procedure. This thermal property can be obtained from the fitting parameter $B=(\pi f/\alpha)^{1/2}$.

The experimental procedure to obtain the optical absorption coefficient, on the other hand, involves plotting the pyroelectric´s signal amplitude (in semi-log scale), as a function of the sample´s thickness, and carry out a fitting procedure. The optical absorption coefficient, in this case, is the slope of the best linear fit.

3. Experimental

3.1 Samples´ preparation

Colloidal gold nano-fluids, at different nano-particle´s sizes (Table I, first column), were obtained starting from a Stock solution of $HAuCl_4$ $3H_2O$, 25 mM in deionized water, at different pH´s. 500 μl of this Stock solution were poured in a 250 ml volumetric flask, with 50 ml of deionized water inside it.

The flask, covered with a watch glass, was put on an electric stove and heated with agitation to bring the mixture to boil, then 1.25 ml of sodium citrate solution ($Na_3C_6H_5O7\cdot 2H_2O$), at 1%, was added very fast, and the mixture was keep heating with agitation up to the nano-particle´s synthesis was complete (about 15 minutes). Sodium citrate worked in this case as a reduction agent and stabilizer at the same time. The pH for each solution was controlled with HCl and NaOH. Nanoparticles´ sizes were characterized by means of atomic force microscopy.

3.2 Photopyroelectric technique for Thermal Diffusivity measurements

The experimental photopyroelectric (PPE) set-up for thermal diffusivity measurements, shown schematically in Fig. 1, consisted of a diode laser with collimation optics (Thorlabs, L785PO90, λ=785 nm), whose light-intensity was modulated by means of a diode current driver (Thorlabs, model LDC202C) controlled by the TTL (Transistor-Transistor-Logic) lockin's output (Stanford Research, model SR 830).

The diode laser with optics was put inside an aluminum cylindrical body and sealed, with epoxy resin, by a thin silicon slab on its bottom (0.02 cm thickness). This set was attached on a micrometer stage with 5 microns of minimum step. The pyroelectric sensor consisted of a PVDF film, 52 microns thickness, with metal electrodes (Ni–Al) on both sides, and 1.5 cm diameter.

The pyroelectric sensor was attached, with a thin layer of conductive epoxy, with the metalized surface of a thin silicon slab (about 200 microns thickness) as a protective layer. The metalized surface of the silicon slab connects the PVDF´s top surface to the metallic body which was the pyroelectric´s electrical ground. The PPE voltage signal generated in the sensor was pre-amplified (Stanford Research systems, model SR-550) and sent to the lock-in amplifier for further amplification and demodulation. The PPE signal was monitored as a function of the sample's thickness L (a sample's thickness scan) in steps of 50 microns and a modulation frequency of 1 Hz, setting the lockin's time constant at 3 s, 15 data points were taken for the analysis.
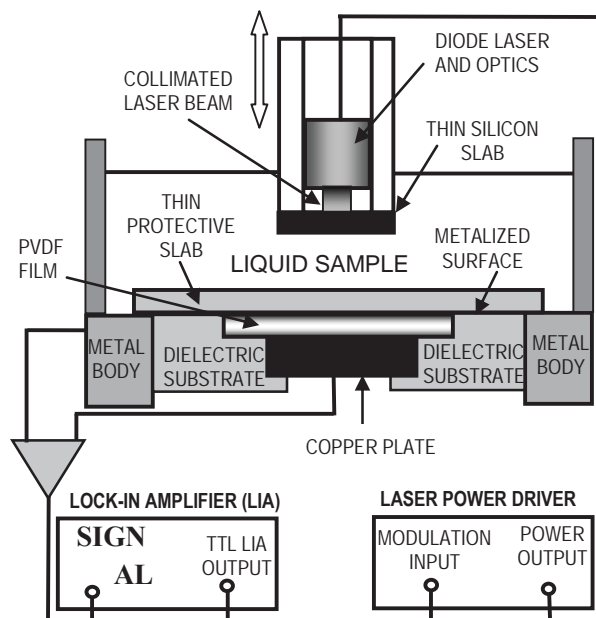

Fig. 1. Cross section of the experimental photopyroelectric set up for thermal diffusivity measurements.

3.3 Photopyroelectric technique for Optical Absorption Coefficient measurements

The experimental photopyroelectric (PPE) set-up for Optical absorption coefficient measurements, shown schematically in Fig. 2, was essentially the one described in section 3.1.

The difference was on the thin silicon slab which was replaced by an optical window, to allow light goes through the liquid sample to be absorbed on its volume.

Three different monochromatic light sources, from lasers, were used this time (commercial laser pointers at 405 nm and 532 nm and an argon ion laser (Spectra Physics), at 488 nm). 30 experimental data points, in steps of 50 microns, were taken for the analysis in this case.
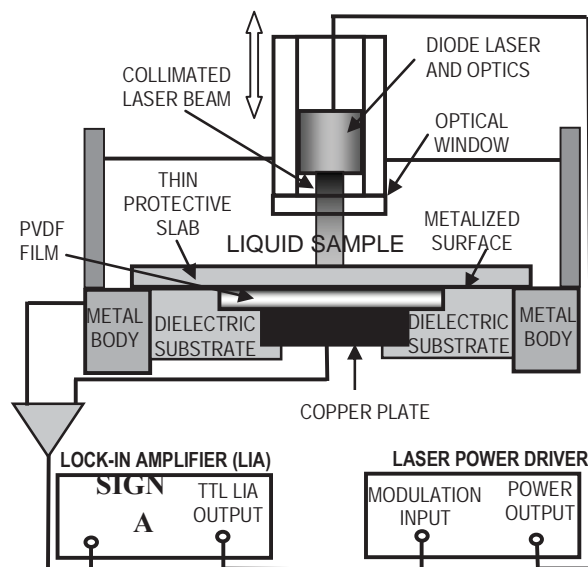

Fig. 2. Cross section of the experimental photopyroelectric set up for optical absorption coefficient measurements.

4. Results and Conclusions

Figure 3 shows typical photopyroelectric signal phases, as function of the sample´s thickness, for two of the gold nanofluids studied in this work (5 nm (Fig. 3a) and 7 nm (Fig. 3b)). The continuous line on each figure is the best linear fit as to obtain the sample´s thermal diffusivity, as it was described before. Table I (column 2) summarize the thermal diffusivity values obtained for all samples.

Figure 4 shows the corresponding photopyroelectric (PPE) signal (a) PPE phase and b) PPE amplitude), as function of the sample´s thickness, for gold nano-particles at 20 nm of dimeter (pH 7). It is evident in Fig. 4a) the constant phase behavior, which validates the corresponding linear fit in Fig. 4b) for the PPE amplitude (in semi-log scale) for obtaining the sample´s optical absorption coefficient at 405 nm, in this case, as it was described in the theoretical section. Similar results are shown on Fig. 5a) for the PPE phase and Fig. 5b) for the PPE amplitude, for the same sample but at a wave-length of 488 nm. Table I, columns 3 to 5, summarizes the corresponding optical absorption coefficients at the three wave-lengths used in this work (405 nm, 488 nm and 532 nm, respectively).

Table 1. Thermo-optical properties for the gold nano-particles studied in this work. α stands for the thermal diffusivity and β for the optical absorption coefficient.

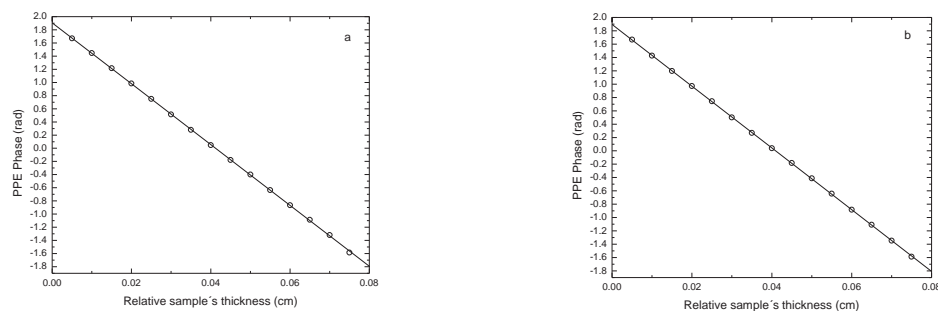| Gold nanoparticle´s diameter (nm)	$\alpha(10^{-2})$ (cm^2/s)	β (405 nm)	β (488 nm)	β (532 nm)
5 (pH 3)	0.1470±0.0008	0.79±0.03	1.56±0.02	1.33±0.03
10 (pH 5)	0.1460±0.0004	1.55±0.04	1.46±0.03	1.13±0.02
20 (pH 7)	0.1466±0.0006	1.75±0.03	1.96±0.02	1.74±0.03
30 (pH 9)	0.1464±0.0007	1.47±0.02	1.55±0.02	1.16±0.04
60 (pH 11)	0.1458±0.0009	1.42±0.05	2.64±0.03	2.07±0.02

Fig. 3. Photopyroelectric (PPE) phase, as a function of the sample´s thickness, for colloidal solution of gold nano-particles. a. 5 nm (pH 3) and b. 20 nm (pH 7). The continuous lines on each figure is the best linear fit as to obtain the sample´s thermal diffusivity.

By looking at the thermal diffusivity values obtained for all samples (Table I, column 2) it is evident that there is no significant difference between these samples in terms of this physical parameter, at least in the range of sizes used in this work. Different conclusions can be reached by looking at the optical absorption coefficients (Table I, columns 3 to 5) since the optical absorption coefficient are clearly different for all samples. It is interesting to note that the greater optical absorption coefficient was measured for the gold nano-fluid at 60 nm and for 405 nm wave-length.

This fact is interesting since the wave-length for strongest absorption for these systems is usually reported around 530 nm, using conventional spectroscopy [4].
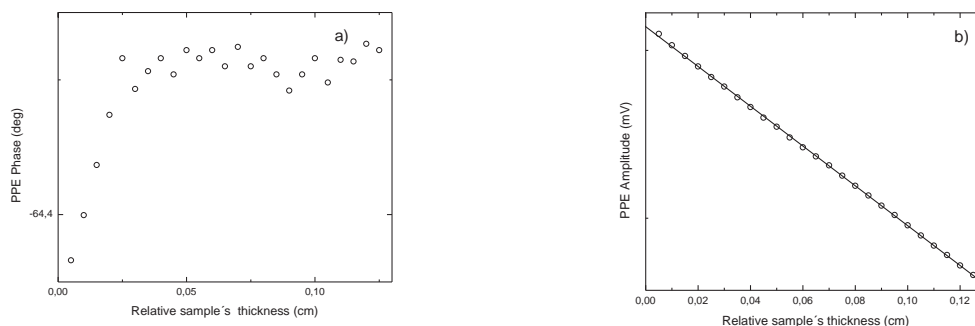

Fig. 4. Photopyroelectric (PPE) signal (a) phase and b) amplitude), as a function of the sample´s thickness, for colloidal solution of gold nano-particles at pH 7. The continuous line on b) is the best linear fit as to obtain the optical absorption coefficient at 405 nm.
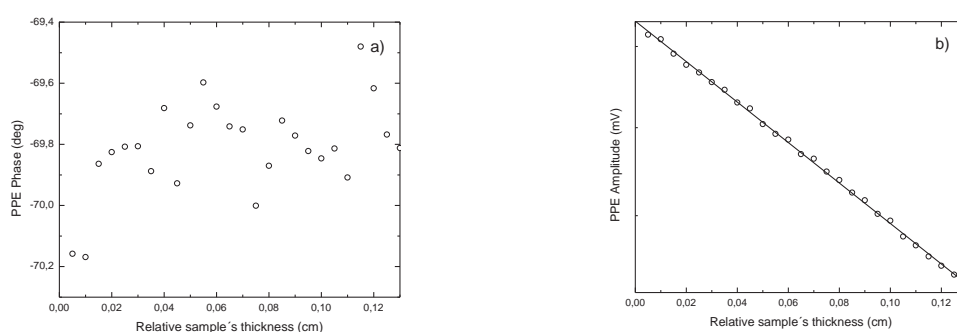

Fig. 5. Photopyroelectric (PPE) signal (a) phase and b) amplitude), as a function of the sample´s thickness, for colloidal solution of gold nano-particles at pH 7. The continuous line on b) is the best linear fit as to obtain the optical absorption coefficient at 488 nm.

References

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