

# Thermal diffusivity measurements in fluids containing metallic nanoparticles using transient thermal lens

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Thermal diffusivity measurements are carried out in water containing gold nanoparticles (~10-40 nm size), using the mode mismatched dual-beam thermal lens technique. An Ar<sup>+</sup> laser is used as the heating source and an intensity stabilized He-Ne laser serves as the probe beam. This technique provides a reliable photothermal alternative for measuring thermal diffusivities of nanofluids and semitransparent samples. The characteristic time constant of the transient thermal lens was obtained by fitting the experimental data to the theoretical expression for transient thermal lens. From this characteristic time it was obtained the fluid thermal diffusivity which increases when the particle sizes increase. The size of nanoparticles was obtained from TEM analysis.

**KEY WORDS:** nanoparticle, nanofluids, photothermal phenomena, thermal lens, thermal diffusivity, transmission electron microscopy

## 1. INTRODUCTION

Thermomodifusivity properties on nanometer scales plays an important role in determining the performance of many state-of-the-art engineering systems. The promise of nanostructured materials for increasing the efficiency of thermoelectric energy conversion, improving heat conduction in composites and heat transfer fluids. Also for targeted thermal effects in medical therapies and photo thermally activated drug delivery, all depend critically on the thermal transport between the nanoparticles and the surrounding liquid [1]. Such nanoparticles may have high light absorbance, and as structural elements of a system that interact with laser radiation, may significantly influence in the thermal diffusivity of the system. Different effects occurring during laser interaction with a nanoscale target, for example the photorefraction effect appears as a laser induced temperature dependent local variation of the refraction index [2-4]. On the basis of this effect, we used Thermal Lens Spectroscopy (TLS) to measure the thermal diffusivity of nanofluids (fluids containing metallic nanoparticles) probes. This technique provides a reliable photothermal alternative for measuring thermal diffusivities of semitransparent materials [5]. TLS technique was also chosen due to its well known potential for avoiding large errors from experimental parameters, and also to its high sensitivity to variation of sample thermal properties. An important advantage of this technique is that, due to the existence of simple linear relation between two measurable parameters, we can directly obtain the thermal diffusivity. Thermal Lens (TL) effect is produced by illuminating a nanofluid with a laser beam with a TEM<sub>00</sub> Gaussian profile; this is the excitation beam. It generates a thermal distribution that induces a proportional change in the refractive index. Such a temperature gradient in the sample gives different optical

path lengths, in a probe laser beam, which passes through the heated space in the sample. The intensity at the center of the probe beam is electronically detected far away from the sample, in this mode. The characteristic time constant of the transient thermal lens was obtained by fitting the experimental data to the theoretical expression for transient thermal lens. We have used the mode mismatched dual-beam thermal lens technique to measure the thermal diffusivity of nanofluids. Using the linear relation between  $t_c$  characteristic time (critical time) and the thermal diffusivity we have obtained the fluid thermal diffusivity. With the help of the complementary transmission electron microscopy (TEM) analyzes it was possible to know the particle average size [1]. A double beam spectrophotometer was used to record the absorption spectra of fluids.

## **2. EXPERIMENTAL SETUP**

Fluids containing Gold (Au) nanoparticles with different sizes were prepared according to the method described by Park *et al.* [6], with some modifications. In a typical synthesis, solutions of  $\text{HAuCl}_4$  (0.096 mmol in 25 ml of water) and poly(N-vinyl-2-pyrrolidone) (PVP, 100 mg in 20 ml of water) were prepared by dissolving the  $\text{HAuCl}_4$  crystals and PVP in water. Both solutions were mixed to produce a Au(III) ion solution containing PVP as a protective polymer. Then an aqueous solution of ascorbic acid (AA, 0.096 mmol in 5 ml of water) was added to the resulting solution at room temperature. A fluid containing metallic particles was formed after the addition of AA solution in the mixture solution. The amount of metal ions was altered from 0.096 to 0.186 mmol in order to control the size of Au particles. The fluids then were diluted to an Au content of 0.033 mmol in 50 ml of water and was placed in a quartz cuvette with 1 cm thick for

the optical and thermal measurements. The experiments were performed at room temperature.

A Shimadzu UV-VIS 3101PC double beam spectrophotometer was used to record the absorption spectra of fluids. Particle sizes and size distribution were evaluated by TEM, using a JEOL-JEM200 microscope. For TEM observations, a drop of fluids was spread on a carbon-coated copper microgrid and dried subsequently in vacuum. Gold particles with average size ranging from 13.9 nm to 37.4 nm were measured. The TL effect of such nanofluids was based on their laser-induced heating and time resolved monitoring on the thermal effects in nanofluids.

The schematic diagram of the TL experimental setup is shown in Fig. 1. An Ar<sup>+</sup> laser, at 514.5 nm wavelength and 40 mW of power, was used as an excitation beam and focused onto the sample with 40 μm of waist radius. The probe beam was a He-Ne laser,  $\lambda = 632.8$  nm and 4mW power with a waist radius onto the sample of 190 μm. An electronic circuit controls a shutter, which consists of a mechanical diaphragm, that was used for limiting the exposure of the sample to the light; when the shutter was opened, the sample was illuminated, and the shutter driver sent a signal to initialize the data acquisition [7]. The maximum intensity of the probe beam was centered on the photodiode detector which signal, as a function of time, was registered and recorded by a Hewlett-Packard 54502A oscilloscope and sent to a PC, through a GPIB interface bus.

### 3. THEORY

We used the aberrant model theory, in the mismatched mode, where the sample is placed in the waist of an excitation laser with a Gaussian spot. From this theory the time evolution of the probe beam intensity ( $I(t)$ ) at the detector is [5]:

$$I(t) = I(0) \left[ 1 - \frac{\theta}{2} \tan^{-1} \left( \frac{2mV}{\left[ (1 + 2m)^2 + V^2 \right] \frac{t_c}{2t} + 1 + 2m + V^2} \right) \right]^2 \quad (1)$$

where:

$$m = \left( \frac{\omega_{1p}}{\omega_e} \right)^2; \quad V = \frac{Z_1}{Z_c}; \quad \theta = - \frac{P_e A_e l_0}{k \lambda_p} \left( \frac{dn}{dT} \right)_p$$

In Eq. (1)  $I(0)$  is the initial value of  $I(t)$ ,  $\theta$  is the thermally induced phase shift of the probe beam after its passing through the sample,  $Z_c$  (12.89 cm) is the confocal distance of the probe beam, and  $Z_l$  (8.0 cm) is the distance from the probe beam waist to the sample;  $\omega_e$  ( $\omega_p$ ) is the spot size of the excitation (probe) laser beam at the sample,  $\kappa(\alpha)$  is the thermal conductivity (diffusivity) of the sample;  $P_e$  is the incident power and  $A_e$  is the optical absorption coefficient at the excitation beam wavelength,  $\lambda_e$ ;  $dn/dT$  is the temperature dependence of the refractive index of sample. The so-called characteristic time of TL,  $t_c$ , is defined as  $D = \omega_e^2 / 4 t_c$  with  $D = k/\rho c$ . Equation (1) describes the time resolved transient that creates the TL effect.

#### 4. RESULTS AND DISCUSSION

Figure 2 presents the UV-Vis absorption spectra of fluids containing Au nanoparticles prepared with different amount of metal ions. An absorption peak around 528 nm was revealed in these fluids, which is generally assigned to the surface plasmon resonance (SPR) of Au nanometric size particles [8]. From this figure we observed that an increase in concentration of Au ions in the mixture solution, corresponds a shift of the optical absorption peak towards higher wavelengths. SPR band position shift are generally assigned to the increase of the Au particles size [8], which agree with the TEM results. Figure 3 shows the TEM images and corresponding size distributions of the Au nanoparticles. Formation of nanoparticles is clear from the TEM micrographs. The average size of the particles ranging from 13.9 to 37.4 nm, is increased with the increase of Au ions in the mixture solution.

The time evolution of TL signal for nanoliquids samples with equal concentration are shown in Fig. 4 to 7, where symbols represent the experimental points and the solid lines correspond to their best fitting to Eq. 1. In Fig. 4 we show the transient thermal lens signal for the nanoliquid at room temperature. The solid line corresponds to the best fitting of the TL experimental data (o) to Eq. (1) leaving  $\theta$  and  $t_c$  as adjustable parameters. Using  $t_c=(\omega_e^2/4 D)$  and having  $\omega_e= 4.0 \times 10^{-3}$  cm, we obtained  $D=(11.42695 \pm 0.16371) \times 10^{-4}$  cm<sup>2</sup>/s, for the thermal diffusivity corresponding to the sample with size 13.9 nm. Figs.5, 6 and 7 show the transient thermal lens signal for nanofluids when the particle sizes increase, from 23.2 nm to 37.4 nm. From the best fitting, of the experimental data to equation 1, it was obtained the thermal diffusivities of the nanoliquid samples which are:  $D=(13.56465 \pm 0.27683) \times 10^{-4}$ cm<sup>2</sup>/s,  $D=(15.70082 \pm 0.37088)$  and  $D=(16.34429 \pm 0.40191) \times 10^{-4}$  cm<sup>2</sup>/s for samples with Au

nanoparticle sizes corresponding to 23.2 nm, 31.5 nm and 37.4 nm respectively. It is possible to see from Figs. 4 to 7 that the signal decreases with time, indicating that thermal lens is divergent, thus defocusing the probe beam on the detector. This behavior is due to the fact that the temperature coefficient of the optical path length,  $ds/dT$ , is negative for most of transparent liquids and plastics. Table I summarizes the thermal diffusivity values obtained from the fitting the experimental data to Eq. 1. It can be seen that there is an increase in the fluid thermal diffusivity when the particle sizes increase.

## **5. CONCLUSION**

TL technique showed its high sensitivity for detecting minimal changes in the thermal diffusivity of liquid samples that contain metallic nanoparticles with different sizes. The obtained results indicates that the golden nanoparticles improve the thermal properties in nanofluids namely the nanoparticles induce local warming. From our results it is possible to a relation between the thermal diffusivity of the nanofluid and the size of the nanoparticle.

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## **ACKNOWLEDGMENTS**

The authors are thankful to the Mexican Agencies, CONACYT, COFAA, CGPI for financial support of this work. One of the author (A. Cruz Orea) is grateful for the partial financial support from CONACYT proyect No. 43252-R. Also J.L. Jiménez Pérez wants to thank the support from CGPI-IPN project No. 20050510.

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## FIGURE CAPTIONS

**Fig. 1.** Schematic representation of the TL experimental setup

**Fig. 2.** Optical Absorption spectra of fluids containing Au nanoparticles prepared with different concentration of metal ions.

**Fig. 3.** Electron micrographs and particle size histograms of Au nanoparticles prepared with different concentration of metal ions: (a) 0.096, (b) 0.126, (c) 0.156 and (d) 0.186 mmol in 50 ml of water. Average Size  $d$  and standard deviations  $\zeta$  are reported.

**Fig. 4.** Time evolution of the TL signal for gold nanoparticles (size of 13.9 nm size). Symbols represent the experimental data and solid line, beneath the points, the best fitting to Eq. (4).

**Fig. 5.** Time evolution of the TL signal for gold nanoparticles (size of 23.2 nm). Symbols (o) represent the experimental data and solid line, is the best fit to Eq. (1).

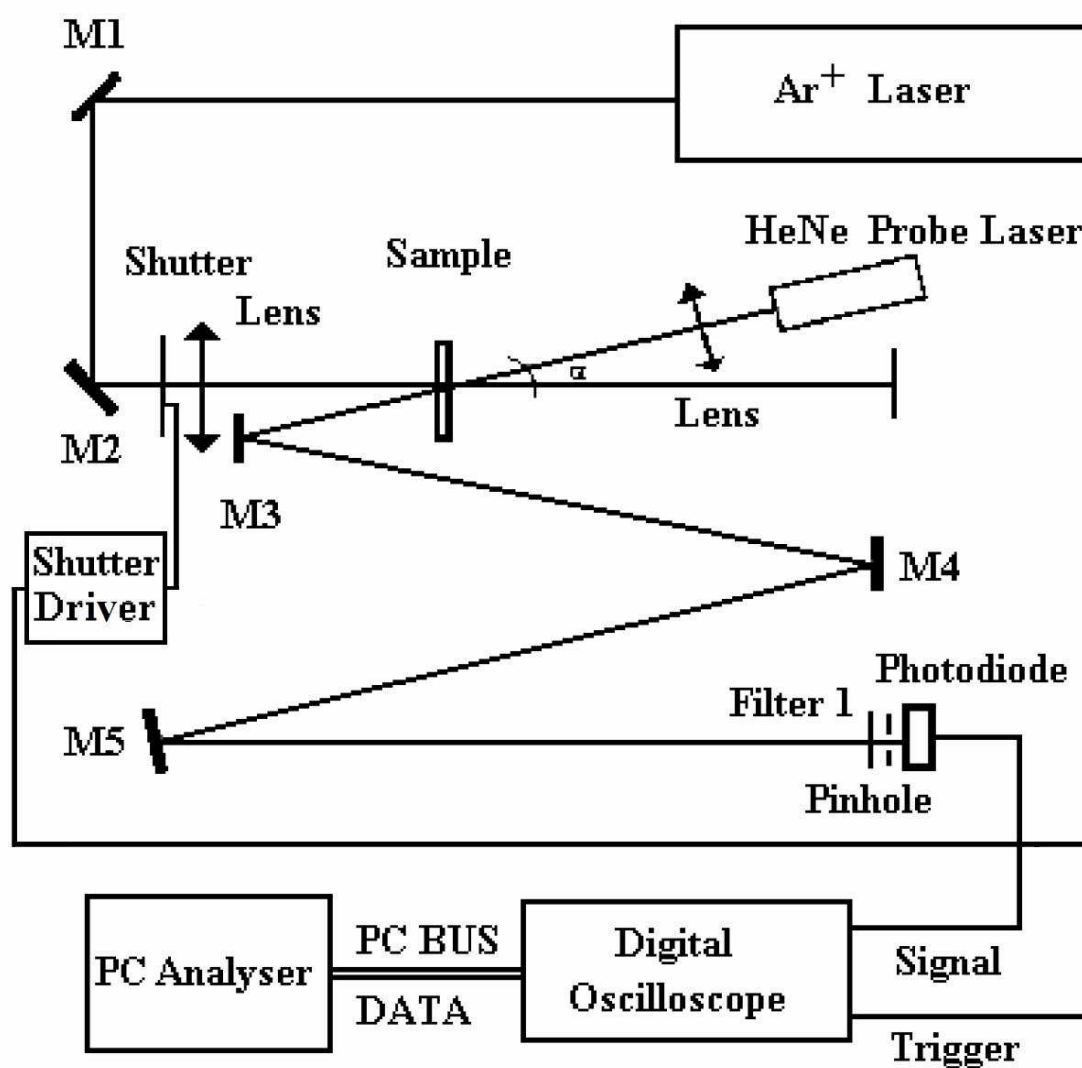
**Fig. 6.** TL signal as a function for gold nanoparticles (31.5 nm size). The experimental data are represent by (o) and solid line, corresponds to, the best fit to Eq. (1).

**Fig. 7.** Time evolution of the TL signal for gold nanoparticles (size of 37.4 nm). Symbols represent the experimental data and solid line, beneath the points, is the best fit to Eq. (1).

**Table I**

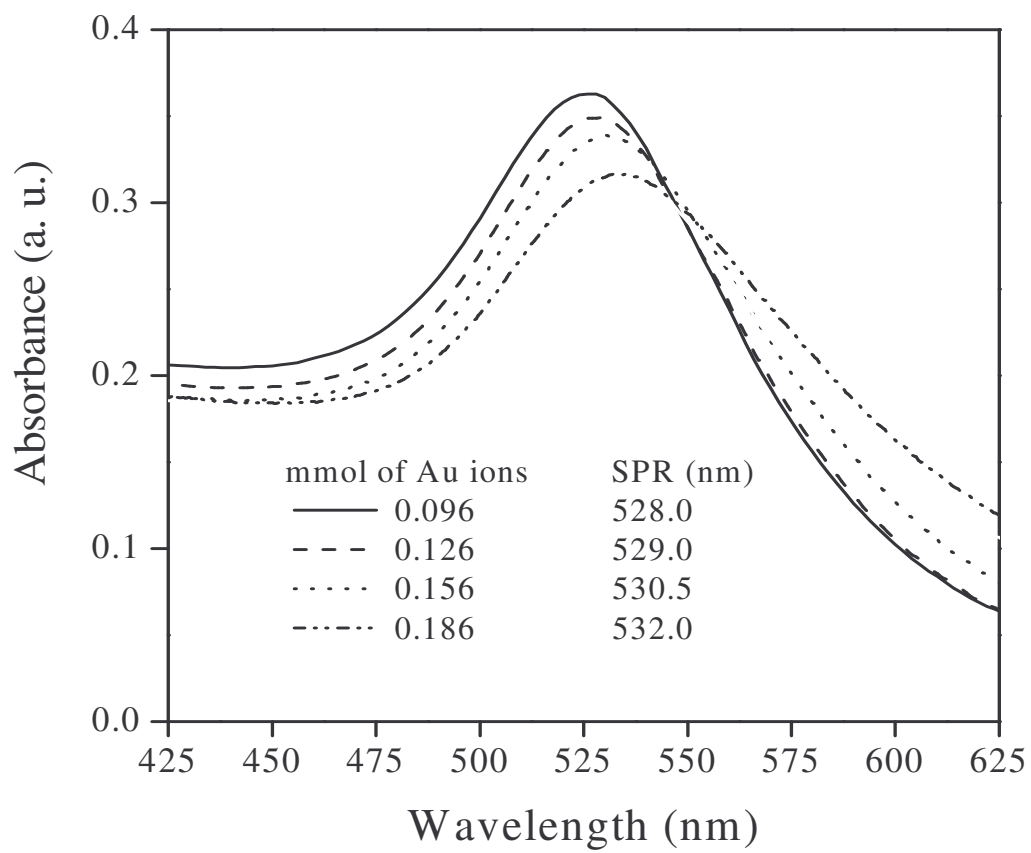
<b>Particle sizes (nm)</b>	<b>tc(s)</b>	<b><math>\theta</math></b>	<b>D(10-4cm<sup>2</sup>/s)</b>
13.9	0.00349±0.00005	0.11962 ±0.00028	11.42695989±0.16371
23.2	0.00294±0.00006	0.10787±0.00032	13.56465646±0.27683
31.5	0.00254±0.00006	0.09801±0.00031	15.70082283±0.37088
37.4	0.00244±0.00006	0.10114±0.00032	16.34429918±0.40191

Fig.1

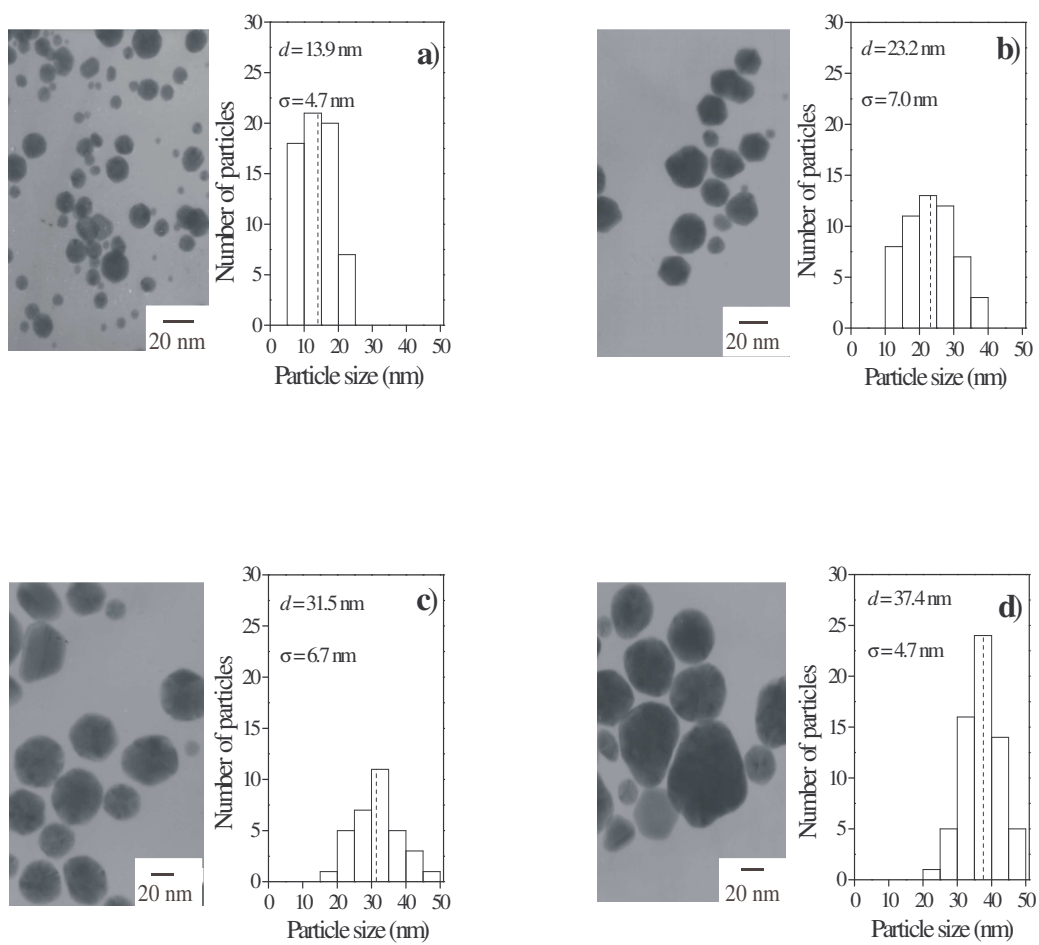


TL experimental set up.

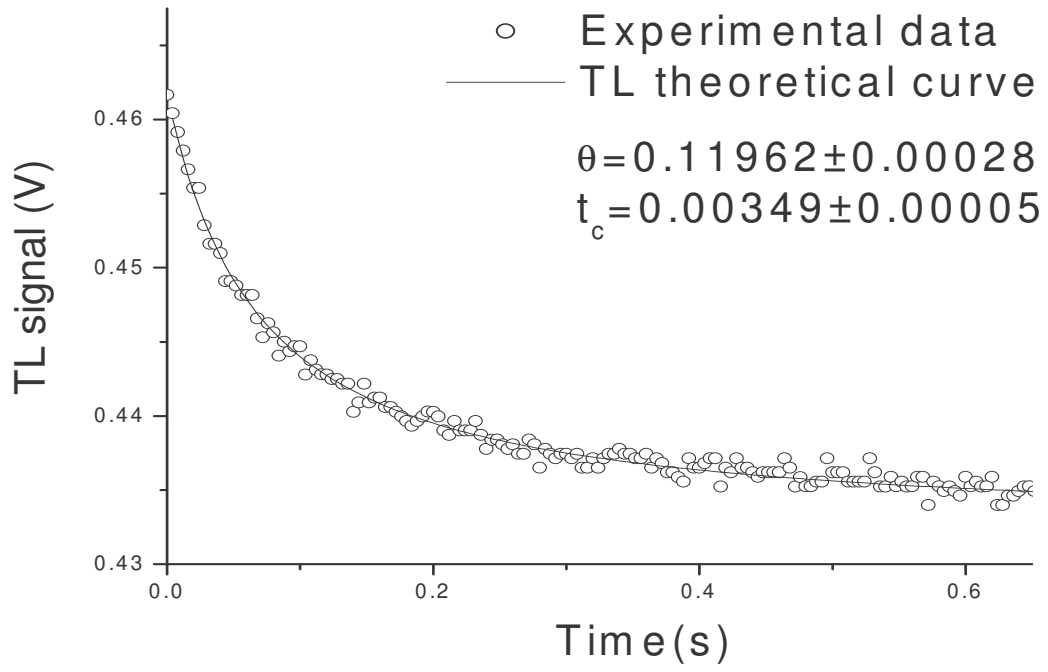
Fig.2



**Fig.3**



**Fig.4**



**Fig. 5**

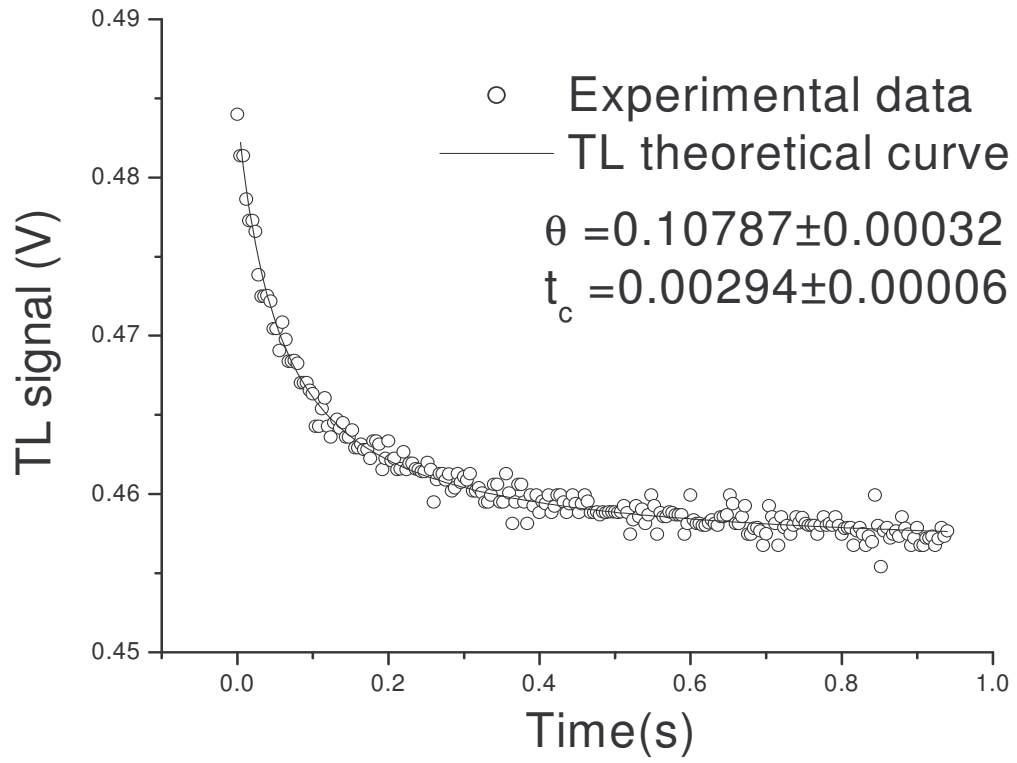
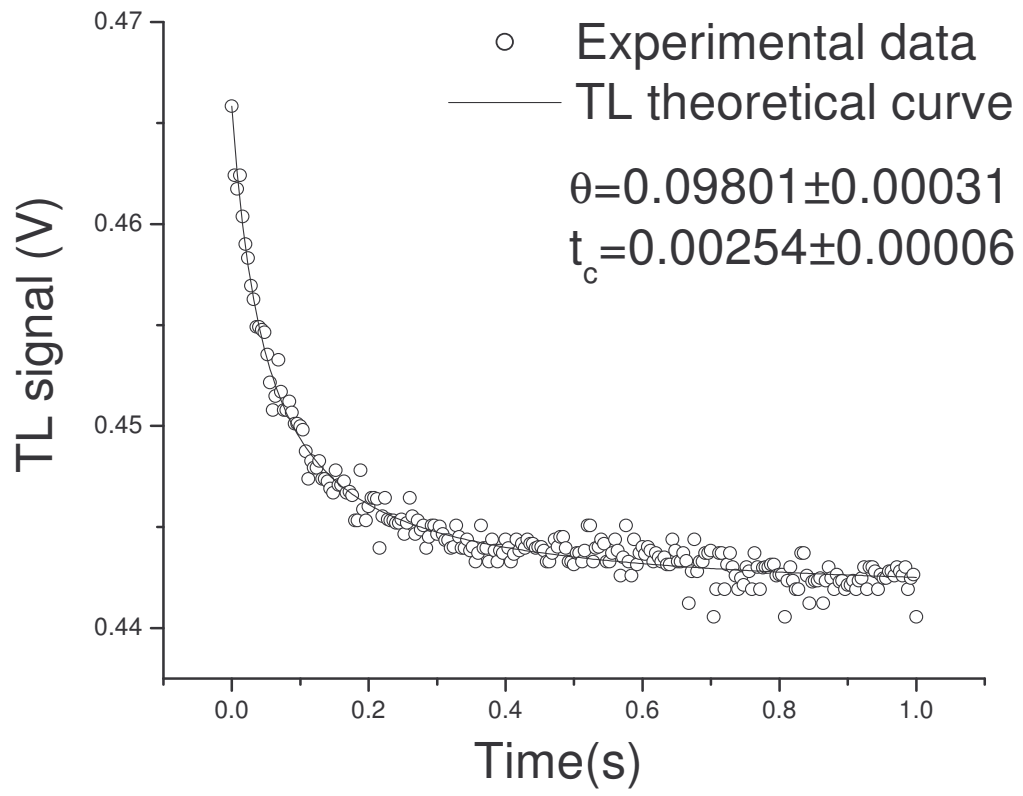


Fig.6





**Fig.7**

