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Variations in thermo-optical properties of neutral red dye with laser ablated gold nanoparticles

Anitha Prakash*, Bini P. Pathrose, S. Mathew, V.P.N. Nampoori, P. Radhakrishnan, A. Mujeeb

International School of Photonics, Cochin University of Science and Technology, Cochin, India

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ABSTRACT

We have investigated the thermal and optical properties of neutral red dye incorporated with different weight percentage of gold nanoparticles prepared by laser ablation method. Optical absorption studies confirmed the production of spherical nanoparticles and also the interactions of the dye molecules with gold nanoparticles. The quenching of fluorescence and the reduction in the lifetime of gold incorporated samples were observed and was due to the non-radiative energy transfer between the dye molecules and gold nanoparticles. Dual beam thermal lens technique has been employed to measure the heat diffusion in neutral red with various weight percentage of gold nano sol dispersed in ethanol. The significant outcome of the experiment is that, the overall heat diffusion is slower in the presence of gold nano sol compared to that of dye alone sample. Brownian motion is suggested to be the main mechanism of heat transfer under the present conditions. The thermal diffusivity variations of samples with respect to different excitation power of laser were also studied.

1. Introduction

Metal nanoparticles have received enormous attention owing to their unique and fascinating optical properties. Among metal nanoparticles, gold nanoparticles (Au) possess several interesting features like facile synthesis and surface modification, strongly enhanced and tunable optical properties and excellent biocompatibility that make them very attractive for intensive research [1,2]. Laser ablation is one of the simple and effective techniques for the production of nanoparticles which does not require any stabilizing or reducing agents and hence purer nanoparticles can be produced [3]. In the present work, Au nanoparticles were synthesized by laser ablation technique using a Q-switched Nd:YAG laser.

The interaction of noble metallic nanoparticles with dye molecules and their impact on the optical properties of fluorescing dye molecules is an important research area in nanotechnology due to their promising applications in diverse fields such as material science, optoelectronics and biomedical applications [4–6]. It was reported that the presence of metal nanoparticles dramatically changes the thermo-optical properties of the samples. Their interaction can result in enhancement or quenching of fluorescence of dye molecules [7–9]. This can be attributed to the resonant energy transfer between a donor molecule and metal nano surfaces with appropriate surface plasmon band, when both are placed in the vicinity of one another [10]. Gold nanoparticles are widely used as quenchers of photo luminescence [11].

Thermal diffusivity is a significant thermo-physical parameter that describes the heat transfer property of a sample by diffusion. A number of methods for determining the diffusivity were discussed in the extensive review of thermal diffusivity of materials by Touloukian et al. [12]. Among the various methods of calculating thermal diffusivity, photoacoustic technique and photo thermal techniques such as thermal lens technique are widely used because of its better sensitivity [13,14]. The thermal lens (TL) method can be successfully employed for the determination of thermal diffusivity, especially in the liquid phase. With a laser of appropriate frequency as the excitation source, a transient thermal lens is produced within the sample, and by monitoring this transient thermal lens we can determine the thermal diffusivity of the sample. The work of Gordon et al. [15] on the thermo-optical effect in a liquid provides a basis for relating the rate of dissipation of the TL to a quantitative measure of thermal diffusivity.

In the present work, we report the variations in optical properties of Neutral Red (NR) dye incorporated with Au nanoparticles prepared by laser ablation method. NR, which belongs to Quinone-Imine class of dyes with molecular formula $C_{15}H_{17}ClN_4$ (Fig. 1), is mainly used for staining cells. It is a lysosomal probe and a biological pH indicator. Because of the high fluorescence, it can also be explored for different applications in optoelectronic field. The thermal diffusivity of NR dye with different weight percentage of Au nanoparticles were measured using dual beam thermal lens technique with ethanol as the base solvent. The temperature dependency in thermal diffusivity values of the

* Corresponding author.
E-mail address: anithaprakash@cusat.ac.in (A. Prakash).

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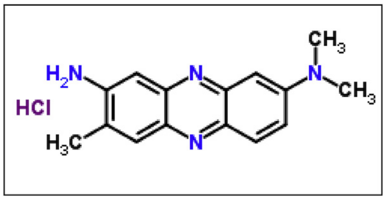

Fig. 1. Molecular structure of Neutral Red dye.

samples was also studied.

2. Theory

Basic experimental technique for thermal diffusivity measurement is to use a focused laser beam of appropriate frequency (pump beam) for exciting the sample. Part of the incident radiation is absorbed by the sample and the non-radiative decay of excited population results in localized heating of the sample. As a result of this heating, a refractive index gradient is created in the sample which behaves as a lens depending on the temperature coefficient of refractive index (dn/dT) of the sample. The thermal lens formed is a divergent one since most of the liquid dyes are having a negative temperature coefficient of refractive index. The thermal lens develops over a period of time governed by the rise time of the excitation pulse and also it is the characteristic of the thermal time constant of the medium. During this time, if one allows another probe beam to pass through the irradiated region and observes the spot at far field, the spot will increase in size, called thermal blooming. That is, the lens diverges the beam and this divergence is detected as a time dependent decrease in power at the center of the beam at far field with the help of an optical fiber - photodetector assembly. The measured intensity is found to be proportional to the thermo-optic parameters of the sample.

The thermal lens technique is based on the measurement of the temperature rise that is produced in an illuminated sample as a result of non-radiative relaxation of the energy absorbed by the sample from a laser. Since the technique is based on direct measurement of the absorbed optical energy, its sensitivity is higher than conventional absorption techniques [16–18]. The thermal lens technique is sensitive enough to measure very small refractive index changes of the order of 10^{-8}, across the beam width resulting from a temperature variation of $\sim 10^{-5}$°C in liquids [19].

The focal length f, of the TL formed in a liquid when a CW laser beam is passed through it at t = 0 is given by,

$$1/f = [P_{abs}\,(dn/dT)] \;/\; [k\pi\omega^2\,(1 + t_c/2t)] \quad (1)$$

Here, P_{abs} is the power absorbed by the liquid, k is the thermal conductivity of the liquid, ω is the beam radius and t_c is the characteristic time for thermal diffusion given by, $t_c = \omega^2\rho c/4k$; where ρ is the density and c is the specific heat. Generally, the excitation power, concentration of the sample, optical path length, etc. should be properly adjusted such that the diverging beam spot is free from aberration rings. Under these conditions, it can be shown that the time-dependent probe beam intensity follows the expression [20],

$$I\,(t) = I_0\,[1 - \theta\,(1 + t_c/2t)^{-1} + (\theta^2/2)\,(1 + t_c/2t)^{-2}]^{-1} \quad (2)$$

Here, the parameter θ is directly proportional to the thermal power degraded as heat P_{th}, the laser wavelength λ_p and other thermo-optic parameters of the material as,

$$\theta = [P_{th}\,(dn/dT)] \;/\; [\lambda_p\,k] \quad (3)$$

The parameters θ and t_c can be obtained by curve fitting of the experimental data to equation (2). With a knowledge of the beam spot size ω at the sample plane, the thermal diffusivity D can be calculated using the formula,

$$D = \omega^2/4t_c \quad (4)$$

3. Experiment

The output of a diode pumped solid state (DPSS) laser emitting at 532 nm with a maximum power of 100 mW was used as the pump beam and a 4 mW Helium–Neon laser emitting at 632 nm was used as the probe beam. The pump beam was intensity modulated using a chopper (frequency 3 Hz). The probe beam was arranged to be collinear with the pump beam and passed through a quartz cuvette of 1 cm path length containing the sample solution through an assembly of a dichroic mirror and a convex lens of focal length 15 cm. The TL effect was detected by monitoring the intensity fluctuations in the beam center of the probe beam. The TL signal was collected using an optical fiber, which is connected to a photodetector–digital storage oscilloscope (DSO) system. A filter was used between the sample and the optical fiber to remove the residual pump and to pass only the probe beam. The schematic of the experimental setup is shown in Fig. 2.

The Gold (Au) nanoparticles were synthesized by pulsed laser ablation technique in which the output of a Q-switched Nd:YAG laser (Spectra Physics Quanta Ray, repetition rate 10 Hz, pulse width 8 ns, maximum pulse energy 1 J) was focused on to a 1 g gold plate of 99.9% purity immersed in ethanol. Before ablation, the plate was washed with deionized water several times to remove impurity from the surface and is placed at the bottom of a beaker filled with ethanol. The Gaussian laser beam of 1064 nm, 100 mJ was focused to the target by a biconvex lens with a focal length of 10 cm for 20 min. During the process of laser ablation, the target was translated manually to confirm uniform

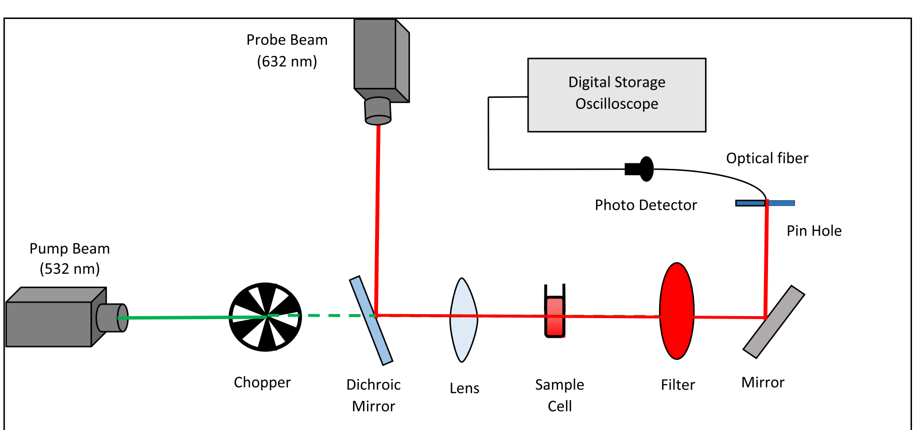

Fig. 2. Schematic of the experimental setup for thermal lens measurement.