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Variations in fluorescence quantum yield of basic fuchsin with silver nanoparticles prepared by femtosecond laser ablation

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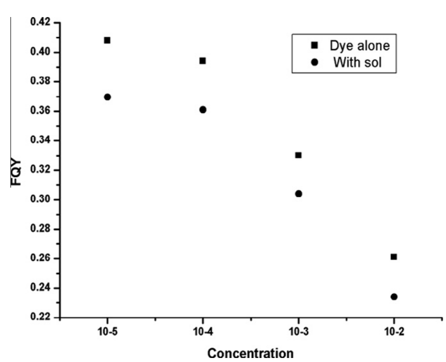
HIGHLIGHTS

- Silver sol is prepared by femtosecond laser.
- Absolute fluorescence quantum yield is calculated using thermal lens technique.
- Quantum yield variations of dye with and without silver sol are plotted.
- The presence of silver sol decreases the fluorescence quantum efficiency.
- The presence of silver sol enhances the thermal lens signal.

GRAPHICAL ABSTRACT



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ABSTRACT

Nano structured noble metals have very important applications in diverse fields such as photovoltaics, catalysis, electronic and magnetic devices, etc. In the present work, the application of dual beam thermal lens technique is employed for the determination of the absolute fluorescence quantum yield of the triaminotriphenylmethane dye, basic fuchsin in the presence of silver sol is studied. Silver sol is prepared by femtosecond laser ablation. It is observed that the presence of silver sol decreases the fluorescence quantum efficiency. The observed results are in line with the conclusion that the reduction in quantum yield in the quenching region is essentially due to the non-radiative relaxation of the absorbed energy. It is also observed that the presence of silver sol enhances the thermal lens signal which makes its detection easier at any concentration.

Introduction

The fluorescence quantum yield (FQY) is defined as the ratio of the number of photons emitted to the number of photons absorbed. Various methods are reported for the determination of FQY of samples [1–7]. The most popular one is the comparative method, by using a fluorescence standard [8]. Such methods are based on the fact that if two substances are studied using the same apparatus and the same incident light intensity, the integrated areas under their corrected fluorescence spectra (S_1 and S_2) are related as

$$\frac{S_1}{S_2} = \frac{\phi_2}{\phi_1}\frac{A_2}{A_1} \tag{1}$$

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where ϕ_1 and ϕ_2 are the corresponding Quantum Yields, A_1 and A_2 are the corresponding absorbance of the two samples, for a particular excitation. The limitation of this method is that it requires a series of suitable standard materials if it is to be used over a wide range of wavelengths. The need of a fluorescence standard can be eliminated if photothermal method like thermal lens technique is adopted [6,7]. Thermal lens technique is a versatile and viable technique for exploring nonlinear processes taking place in organic materials [9], dyes [10], dye mixtures [11] and metallic colloids [12]. It is a highly sensitive method, capable of giving absolute values of FQY with high accuracy and reproducibility. The absolute values of FQY of laser dyes are important for the calculation of thresholds of laser action. The thermal and fluorescence spectroscopy used to measure FQY are complementary to one another: the former measures the photon energy, which is converted into heat, and the latter observes re-emitted photons. The thermal fluctuations produced by the non-radiative relaxation results in density variations which lead to refractive index variations. A lens is created through the temperature dependence of the sample refractive index and the phenomenon is called thermal lensing. For most of the liquids, the temperature coefficient of refractive index is negative and hence the thermal lens signal generated is divergent.

Noble metal nanoparticles have unique size-dependent optical, magnetic and catalytic properties [13–15]. Because of these properties silver nanoparticles are used for applications in various areas such as catalytic, optical and antibacterial applications [16,17]. In order to produce pure nanoparticles, and to eliminate surfactant for capping of colloidal nanoparticles laser ablation method is commonly used [18–20]. The FQY and photoluminescence spectra can be altered in the presence of nanoparticles. Association of metal nanoparticles with dye molecules results in enhancement or quenching of fluorescence of dye molecules [21]. The quenching of fluorescence is due to the increase in the nonradiative decay and enhancement of fluorescence is due to the increase in excitation decay rate caused by the plasmon field created around the nanoparticles by the incident radiation [22]. Association of silver nanoparticles with Rhodamine6G increases the photoluminescence quenching and hence FQY is reduced [17,23]. It is reported that quantum yield and photoluminescence spectra of CdSe/ZnS core–shell quantum dots suspended in toluene and tetrahydrofuran solvents are independent of the excitation wavelength [24]. In the present study, a femtosecond laser is utilized to generate silver nanoparticles in ethanol.

Basic fuchsin (BF) is a triaminotriphenylmethane dye with molecular formula $C_{20}H_{20}ClN_3$ (Fig. 1). It is a mixture of three dyes Pararosaniline, Rosaniline, and Magenta II and is known as Magenta II. This dye is inflammable in nature and possesses anesthetic, bactericidal (gram positive), and fungicidal properties. It is widely used as coloring agent for textile and leather materials, staining of collagen, muscle, mitochondria, and tubercle bacillus. The present paper describes the effect of silver nanoparticles on the FQY of fuchsin dye.

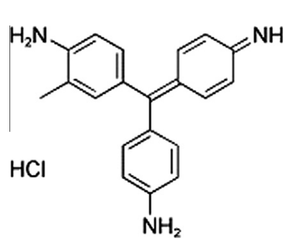

Fig. 1. Molecular structure of basic fuchsin.

Experimental

The experimental set up (Fig. 2) used is similar to the one reported by Fang and Swofford [25]. A diode pumped solid state (DPSS) laser emitting at 532 nm having a maximum power of 100 mW is used as the pumping source and a low power Helium–Neon laser (Spectra Physics-5 mW, 632 nm) is used as the probe beam. The pump beam is intensity modulated using a chopper (frequency 3 Hz) and the probe beam is made collinear and passed through a quartz cuvette containing sample solution through an assembly of dichroic mirror and convex lens (focal length 20 cm). The absorption coefficient of fuchsin basic at 632 nm is very narrow as compared to that of the pump beam and hence the perturbation in refractive index due to probe beam can be neglected. The thermal lens signal generated is filtered to allow the passage of signal at 632 nm only. After filtering, the thermal lens signal is then collected with the help of an optical fiber which in turn is connected to a monochromator–PMT–Digital Storage Oscilloscope assembly. Optical density filters were used in between the pumping source and sample to vary the laser intensity. In the present study a power output of 80 mW from a DPSS laser is used for heating the sample.

Silver nanoparticles were prepared by pulsed laser ablation of a silver plate of thickness 1 mm having purity of 99.99%. The plate was polished, and then washed with deionized water several times to remove impurity from the surface. The silver plate was placed at the bottom of a culturing dish filled with 15 ml of ethanol. The laser system was a femtosecond pulsed laser which consists of a femtosecond laser seed (Tsunami (Mode-locked Ti: sapphire Laser), 700 mW, 800 nm, about 100 fs, 80 MHz) and a regeneration amplifier (Spitfire Pro). The output laser had a repetition at 1 kHz with pulse width of 120 fs and wavelength of 800 nm. During the procedure of laser ablation, the target was rotated manually to ensure uniform ablation and to avoid texturing effect. The Gaussian laser beam was focused by a biconvex lens with a focal length of 5 cm to the target, which was immersed in ethanol.

The amplitude and frequency of the surface Plasmon resonance (SPR) peak depends on the nature of metal, shape and size of the particles, nature of the solvent and particle density [26]. The size and shape of nanoparticles can be qualitatively described by the peak position and shape of the absorption spectrum [27]. It is observed that the absorption peak of silver nanoparticles is having a single peak is and is located around 404 nm (Fig. 3).

The sample solution is prepared by an accurately weighed amount of dye and dissolving it in ethanol to obtain samples of various concentrations from 10^{-2} mol/L to 10^{-5} mol/L. To these samples an appropriate amount of 10^{-4} mol/L silver sol is added.

Theory

The fluorescence quantum yield Q_f is the ratio of the number of photons emitted as fluorescence to the number of photons absorbed. The method is based on the principle of energy conservation. Let P_0 be the power of the incident beam, P_t be the power of the transmitted beam, P_f be the emission power and P_{th} be the power dissipated as heat. In the absence of any photochemical reaction the absorbed power can be written as a sum of transmitted power, thermal power degraded to heat and the emission power as given by Eq. (2).

$$P_0 = P_{th} + P_f + P_t \quad (2)$$

Assuming reflection and scattering losses to be negligibly small, the transmittance can be written as

$$T = \frac{P_t}{P_0} \quad (3)$$