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Non-Linear Optical Properties for Thin Films of Fluorescein Organic Laser Dyes Doped with Polyvinyl Alcohol Polymer and Al_2O_3 Nanoparticles †

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Abstract: This article presents a comprehensive study on the optical properties of fluorescein dye doped with PVA polymer and Al_2O_3 nanoparticles. The investigation covers the material's absorbance behavior, surface morphology, and nonlinear optical characteristics. Through the use of UV-VIS spectrometry and AFM, the study demonstrates how doping affects the dye's absorption spectrum and grain size on the surface. The application of the Z-scan technique further allows for the measurement of the nonlinear refractive index and absorption coefficient, revealing self-defocusing lensing and distinguishing the absorption phenomena in both solutions and thin films. The results underscore the potential of fluorescein-based materials in the development of advanced optical devices, offering valuable insights for future research in material science and photonics.

Keywords: fluorescein dye; PVA polymer; Al_2O_3 nanoparticles; UV-VIS spectrometry; AFM; Z-scan technique; nonlinear optical properties; two-photon absorption; saturable absorption; optical devices

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1. Introduction

Large organic molecules constitute the active materials in laser dyes [1]. When dissolved in suitable solvents such as ethanol, methanol, or an ethanol–water mixture, these organic molecules can function as the lasing medium in dye lasers [2]. Laser dyes are characteristically complex molecules, often featuring multiple ring structures, which contribute to their intricate absorption and emission spectra [3]. Depending on their chemical structures, laser dyes can be categorized into various classes, with coumarins, xanthenes, and pyrromethenes being typical examples [4]. The significant long-wavelength absorption band of these dyes is due to the electronic state transition from the ground state (S_0) to the first excited singlet state (S_1), characterized by a high transition moment and an oscillator strength close to unity. The reverse transition from S_1 to S_0 is the source of spontaneous emission in dye lasers [5]. In applications, laser dyes serve as the active media in both pulsed and continuous-wave (CW) dye lasers and are utilized as ultrafast shutters for Q-switching and passive mode-locking, necessitating a diverse range of dyes to span the complete spectral range [6]. The use of dye mixtures as a lasing medium is primarily motivated by the enhancement of laser performance and the capability for multi-frequency operation [7]. This study investigates the nonlinear optical properties of fluorescein organic laser dye doped with polyvinyl alcohol (PVA) polymer and aluminum oxide (Al_2O_3) nanoparticles. These dyes were dissolved in ethanol at varying concentrations of 1×10^{-5}, 3×10^{-5}, 5×10^{-5} and 7×10^{-5} M and analyzed at room temperature.

2. Theory

The theoretical framework for evaluating the optical properties of dye solutions begins with the determination of the linear absorption coefficient (α_o), which is derived from Equation (1) [8–10]:

$$\alpha_o = \frac{\ln(1/T)}{t} \tag{1}$$

where t represents the thickness of the sample, and T is its transmittance. Additionally, the refractive index (n_o) is a critical parameter that can be deduced from the transmittance spectrum of the film, as per Equation (2) [10]:

$$n_o = \frac{1}{T} + \left(\frac{1}{T^2} - 1\right)^{1/2} \tag{2}$$

Transmittance, denoted as $T\%$, indicates the percentage of incident light that the solvent allows to pass through [11]. For instance, a 50% transmittance means that half of the incident light is transmitted through the solution [12]. This can be quantified by Equation (3):

$$T\% = \left(\frac{I}{I_o}\right) \times 100\% \tag{3}$$

where I_o is the intensity of the incident light, and I is the intensity of the transmitted light. The interrelation between transmittance (T) and absorbance (A) is articulated through Equation (4) [12]:

$$A = \log_{10}\left(\frac{1}{T}\right) \tag{4}$$

3. Materials and Methods

Fluorescein, belonging to the xanthene class of dyes, is characterized by its high chemical stability, which is influenced by the polarity of the solvent. It typically appears as an orange-red to dark crystalline powder [13]. Its applications are diverse, ranging from being a fluorescent tracer in technical chemistry, microscopy, serology, and forensics to its use in medical diagnostics, such as in surgery for brain tumors, angiography, and ophthalmology [14–16]. Fluorescein is also utilized for its sterile properties, with the molecular formula $C_{20}H_{12}O_5$, as depicted in Figure 1. Solutions with a concentration of 10^{-4} M were prepared using fluorescein dye in ethanol solvent. An electronic balance (BL 210 S, Sartorius, Goettingen, Germany) with four-digit sensitivity was employed to weigh the powder. Various concentrations (1×10^{-5}, 3×10^{-5}, 5×10^{-5}, and 7×10^{-5} M) were prepared using Equation (5) [17]:

$$W = \frac{M_w \times V \times C}{1000} \tag{5}$$

where W is the weight of the dye (g), M_w is the molecular weight of the dye (g/mol), V is the volume of the solvent (ml), and C is the concentration (M). The solutions were subsequently diluted according to Equation 6 [18]:

$$C_1V_1 = C_2V_2 \tag{6}$$

where C_1 and C_2 are the initial and final concentrations, respectively, and V_1 and V_2 are the volumes before and after dilution, respectively.

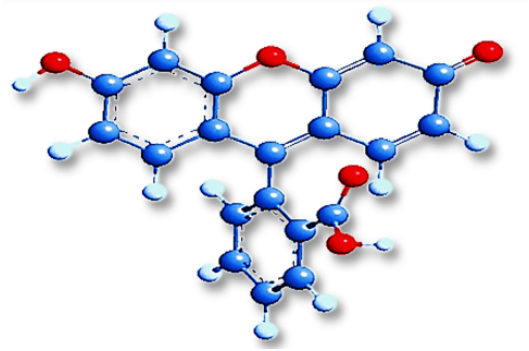


Figure 1. Molecular structure of fluorescein organic dye.

4. Results and Discussion

Atomic force microscopy (AFM), one of the proven technique [19,20], was utilized to analyze the surface topology of thin films of fluorescein dye doped with PVA polymer and Al_2O_3 nanoparticles at a concentration of 10^{-3} M. Figures 2 and 3 illustrate the two-dimensional (2-D) and three-dimensional (3-D) images, respectively, providing insights into the distribution of granular growth groups on the surfaces of the deposited films. As indicated in Table 1, there is a discernible increase in both the average grain size and the root mean square (r.m.s) of surface roughness with an increase in film thickness for both undoped and doped fluorescein (FL) thin films [6].

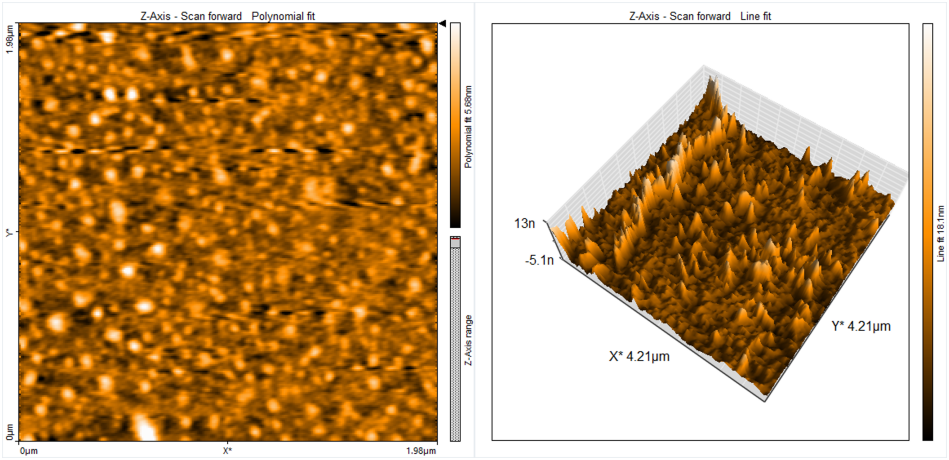


Figure 2. Two-dimensional and three-dimensional AFM images for thin films of fluorescein dye doped with PVA polymer.

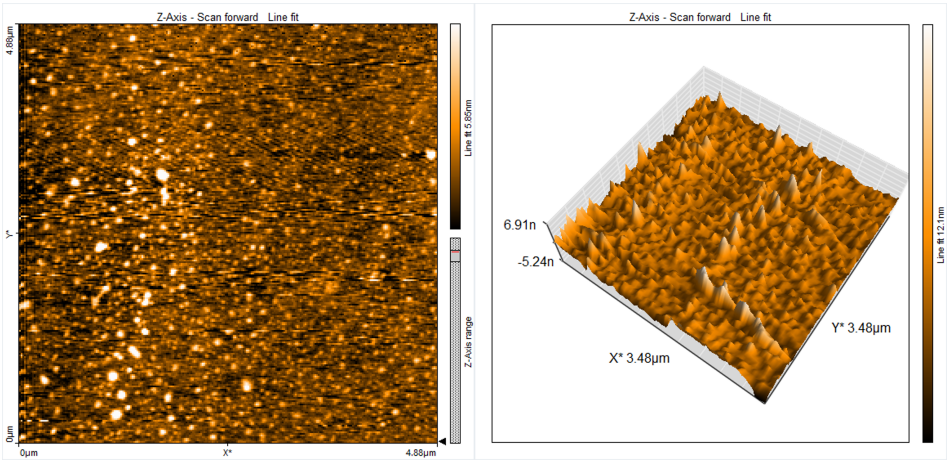


Figure 3. Two-dimensional and three-dimensional AFM images for thin films of Fluorescein doped with PVA polymer and Al_2O_3 NPs.

Table 1. AFM parameters for fluorescein doping with PVA polymer and Al_2O_3 NPs.

Material	r.m.s (nm)	Roughness (nm)	Average Grain Size (nm)	Thickness (nm)
FL+PVA polymer	8.688	5.552	51	146
FL+PVA polymer + Al_2O_3 NPs	9.211	6.664	59	155

The absorbance spectra of the fluorescein organic laser dye at various concentrations (1×10^{-5}, 3×10^{-5}, 5×10^{-5}, and 7×10^{-5} M) in ethanol were recorded over a wavelength range of 190 to 1100 nm using a UV-VIS spectrometer (Aquarius 7000, Optima, Tokyo, Japan), at room temperature, and are displayed in Figure 4. This figure reveals a broad spectral absorption range for the fluorescein solution between 328 nm and 530 nm. An increase in concentration, and thus an increase in the number of molecules per unit volume, enhances absorbance, which in turn affects the energy states, resulting in an elevation of both the linear absorbance index and refractive index, as well as a reduction in transmittance. These findings are consistent with the Beer–Lambert law [21].

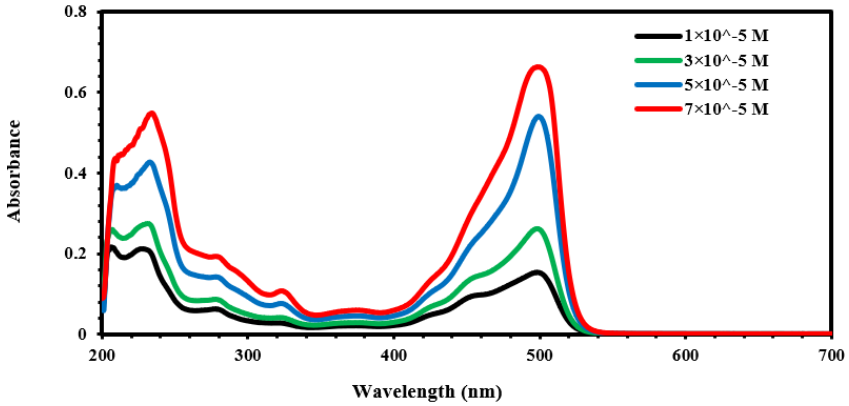


Figure 4. Absorbance spectra for fluorescein dye at different concentrations in ethanol solvent.

Figure 5 depicts the linear absorbance spectra of thin films of Fluorescein dye at a concentration of 10^{-3} M, doped with PVA and Al_2O_3 nanoparticles. The absorption peaks of the doped films show a redshift towards longer wavelengths compared to the pure dye. This shift can be attributed to changes in the electronic and vibrational states of interfacial molecules, leading to enhanced absorption across all nanocomposite samples. This is hypothesized to occur due to the excitation of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

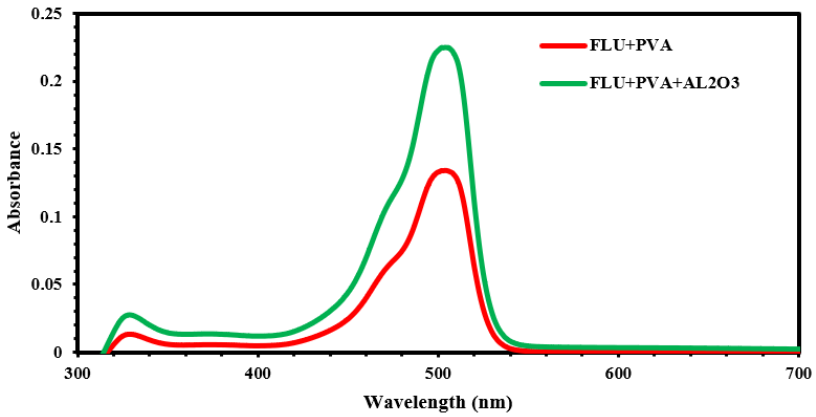


Figure 5. The absorbance spectrum for thin film of fluorescein organic laser dye doped with PVA polymer and (Al_2O_3) NPs.

The linear refractive coefficient (n_o) and linear absorption coefficient (α_o) were calculated for all samples using Equations (1) and (2), respectively, as detailed in Tables 2 and 3. The maximum absorption wavelength for fluorescein was identified at 497 nm.

Table 2. Materials and their respective concentrations.

Material	Concentration (Mol/L)
Fluorescein (solutions)	1×10^{-5}
Fluorescein (solutions)	3×10^{-5}
Fluorescein (solutions)	5×10^{-5}
Fluorescein (solutions)	7×10^{-5}
FL+PVA polymer (thin films)	1×10^{-3}
FL+PVA polymer + Al_2O_3NPs (Thin films)	1×10^{-3}

Table 3. Optical parameters for different materials at $\lambda = 457$ nm.

Material	T	α_o (cm^{-1})	n_o	$\Delta TP - V$	n_2 (cm^2/mW)	β (cm/mW)
Fluorescein (solutions)	0.8016	0.2210	1.2931	0.0277	3.5016×10^{-11}	1.2947
Fluorescein (solutions)	0.7194	0.3293	1.4955	0.0361	5.5024×10^{-11}	1.4198
Fluorescein (solutions)	0.5760	0.5515	1.7849	0.0416	7.6834×10^{-11}	1.5068
Fluorescein (solutions)	0.4714	0.7519	1.9216	0.0527	8.5168×10^{-11}	1.6264
FL+PVA polymer (thin films)	0.6748	6396.33	1.1652	0.132	2.91×10^{-7}	2.023
FL+PVA polymer + Al_2O_3NPs (thin films)	0.6402	6806.97	1.1852	0.154	3.89×10^{-7}	3.765

Continuing the exploration of optical properties, Z-scan experiments were conducted using a continuous-wave (CW) diode solid-state laser operating at a wavelength of 457 nm and a power of 84 mW. The laser beam was focused through a lens with a 15 mm focal length. The experimental setup is diagrammatically represented in Figure 6. In the setup, a 1 mm wide optical cell containing a solution of mixed organic dyes in ethanol solvent at varying ratios was translated through the focal region along the axial direction, coinciding with the direction of the laser beam's propagation.

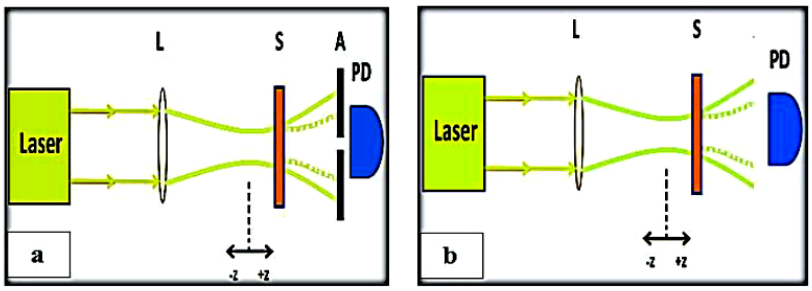


Figure 6. (**a**) Closed-aperture Z-scan; (**b**) open-aperture Z-scan [21].

The Z-scan technique is employed in two variants: the closed-aperture method, which is used to determine the nonlinear refractive coefficient (n_2); and the open-aperture method, which ascertains the nonlinear absorption coefficient (β). In the closed-aperture configuration, the far-field intensity pattern is measured as a function of the sample's position by observing the transmittance changes through a small aperture placed at the far-field location. By analyzing the transmittance variation with the Z-scan measurements, the third-order nonlinear refractive coefficient (n_2) and the nonlinear absorption coefficient (β) were determined for all samples in ethanol solvent across different mixing ratios [21]. The Z-scan method is instrumental for quantifying the nonlinear optical properties of materials, specifically the nonlinear refractive index (n_2) and the nonlinear absorption coefficient (β). It employs both open- and closed-aperture techniques to measure these parameters. The

normalized transmittances from Z-scan measurements, plotted as a function of the sample's position relative to the focal point, are illustrated for fluorescein dye in ethanol solvent in Figures 7–10. The nonlinear effect region, as demonstrated in these figures, extends from −2 mm to 2 mm from the focal point.

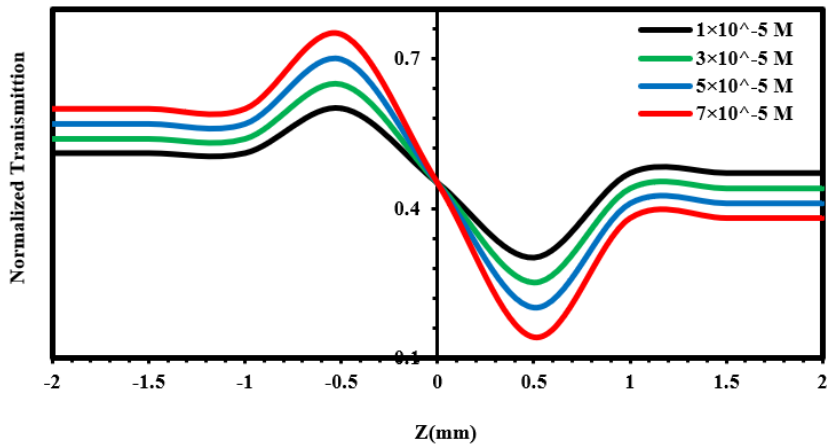


Figure 7. Closed-aperture Z-scan data for different concentrations of fluorescein organic laser dye in ethanol solvent.

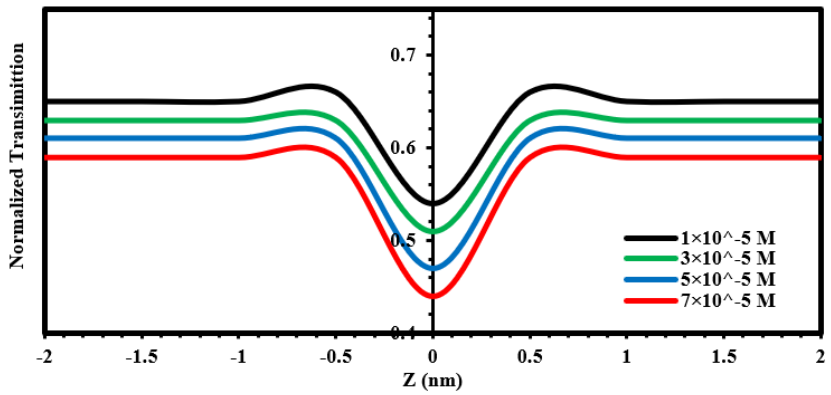


Figure 8. Open-aperture Z-scan data for different concentrations of fluorescein organic laser dye in ethanol solvent.

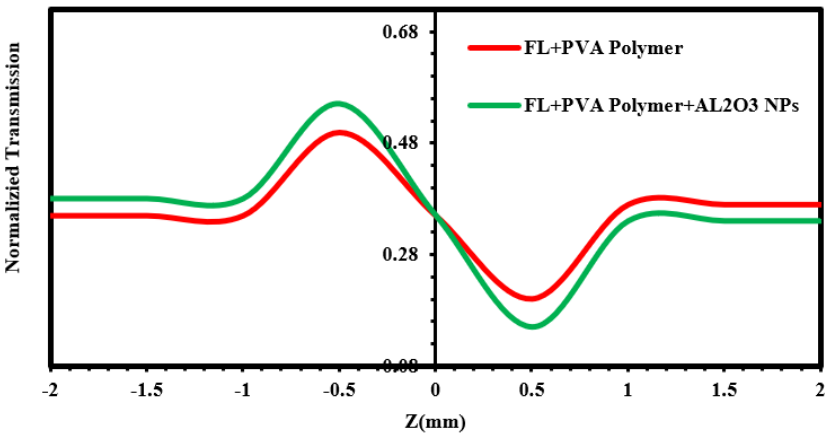


Figure 9. Closed-aperture Z-scan data for thin films of fluorescein organic laser dye doped with PVA polymer and (Al_2O_3) NPs.

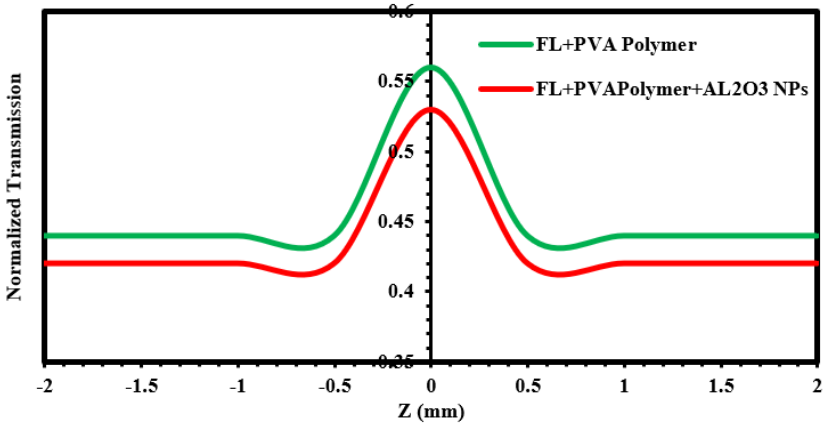


Figure 10. Open-aperture Z-scan data for thin films of fluorescein organic laser dye doped with PVA polymer and (Al_2O_3) NPs.

The characteristic peak followed by a valley in the transmittance curve, derived from closed aperture Z-scan data, signifies a negative nonlinear refractive index ($n_2 < 0$), indicative of self-defocusing phenomena within the sample [21], as depicted in Figures 8 and 10. Conversely, open-aperture Z-scan data reveal different behaviors for solutions and thin films.

For fluorescein organic laser dye in solution, two-photon absorption phenomena are observed, as shown in Figure 9. In the case of thin films, the data indicate saturable absorption, which is presented in Figure 10.

5. Conclusions

In summary, the study has successfully elucidated the intricate optical properties of Fluorescein dye when doped with PVA polymer and Al_2O_3 nanoparticles. The absorbance spectra and surface morphology, analyzed through UV-VIS spectrometry and AFM, respectively, have provided substantial insights into the material characteristics. Particularly, the Z-scan technique has proven to be a pivotal method for assessing the nonlinear optical parameters, revealing negative nonlinear refractive indices indicative of self-defocusing phenomena and distinguishing between two-photon and saturable absorption in solutions and thin films, respectively. These findings not only contribute to the existing body of knowledge regarding the nonlinear optical behavior of organic compounds but also pave the way for potential applications in optical devices where such properties are requisite. Future work may focus on exploring the influence of varying nanoparticle sizes and concentration ratios, aiming to fine-tune these optical properties for specific technological applications.

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