The Plasmon Effects of AgNPs on Wave Guide Consisting of Polymers Mixed with Rhodamine Dyes

S A Suheil, N S Shnan and Qussay Mohammed Salman

Department of Laser physics, Science Collage for Women, Babylon University, IRAQ.

E-mail: aldwahsnds@gmail.com, nizarflifl@yahoo.com, qusay63@yahoo.com

Abstract. In this research, the optical properties refractive index, absorption spectrum, and fluorescence spectrum of solutions of different concentrations have been studied in order to prepare thin films to obtain an efficient waveguide. A wave guide consisting of three layers has been prepared in which the middle layer has a relatively higher refractive index than the upper and lower layers. This optical wave guide was prepared by using different solutions of two concentrations of poly vinyl pyrrolidone (PVP) & poly vinyl alcohol (PVA) polymers. Different concentrations of the rhodamine pigments RhB & Rh6G were prepared. It is added to the middle layer of the optical wave guide in order to raise its refractive index first and to obtain a laser profit. The practical results have proven that there are specific concentrations of polymers and dyes that can be used to obtain wave guides that have the ability to transmit and amplify the input signal and operate within certain wavelengths. The PVA + RhB(10-4M) model showed the best laser emission performance and the PVA + Rh6G (10-5M) model showed the best signal transmission performance. Finally, the plasmon effect is clearly appears when we added the AgNPs on our samples it’s effecting on threshold pumping and increase the efficiency of wave guide.

Keywords: Polymers, Rhodamine, waveguide, refractive index, fluorescence spectra, pulse energy, Plasmon.

1. Introduction

An optical polymer waveguide is made of materials. It has a centric core where the light is transmitted[1] surrounded with an outer cladding of a little lower index of refraction[2]. Rays of the light that incident on a core- cladding limiting with an angle which is 90 bigger than the critical angle that undergoes the total internal reflection and limited inside the core without any refraction [3]. The material of which a polymer waveguide is made must be transparent to optical wavelengths[4]. Polymer waveguides doped with (RhB, Rh6G) dyes for active elements (lasers and amplifiers) because of the high refractive[5]. Polymer waveguides are formed by spin- coating a polymer solution onto a substrate, forming a circuit pattern, and then spin-coating another dye added to polymer layer on top for planarization[6]. By controlling the polymer/solvent ratio and the spin speed of film coating, film thickness can be obtained in the range from 0.1 to 100 um[7]. The core layer is vaccine by adding to silver nanoparticles Where have a great role in achieving the phenomenon of surface plasmon resonance (SPR)[8] is the manifestation of a resonance effect due to the interaction of conduction electrons of metal nanoparticles with incident photons[9]. The interaction relies on the size and shape of the metal nanoparticles and on the nature and composition of the dispersion medium[10]. Plasmonic
nanostructures have been proposed as a new efficient heat source when illuminated by their correspondence resonance light source [11, 12] regarding the nanoscale control of temperature distribution [13] drug delivery [14, 15] cancer photo-thermal therapy [16, 17] photo-thermal imaging [18] and various other useful applications. These applications should be capable of measuring the temperature distribution in a sufficient area with a high signal-to-noise ratio (SNR) [19]. The advantage of polymer waveguide spectrometers is the lack of loss during the reflection of light inside the wave guide the disadvantage is the absorption loss inside the waveguide, which makes it impossible to use this kind of spectrometer in the infrared range. This kind of spectrometer is therefore well suited for the analysis of light in the UV and visible range advantage of polymer waveguide Bandwidth is higher than copper cables. Less power loss and allows data transmission for longer distances. The optical cable is resistance for electromagnetic interference. The size of the fiber cable is 4.5 times better than copper wires [20].

2. Experimental part

2.1. Dyes, polymers and solvents used
In this research, two types of xanthine dyes were used, and the following are described: Rhodamine dye (Rh6G) looks like a red solid powder, and dissolves in water, alcohol and ethanol to form a fluorescent orange solution, and its chemical formula is \( \text{(C}_{28}\text{H}_{31}\text{N}_{2}\text{O}_{3}\text{Cl)} \), and its molecular weight is (479.02 gm / mole) [21] when this dye is dissolved in water it has a purity is about (99%). Another dye was used which is the Rhodamine dye (RhB). This dye consisting of green solid crystals or in the form of a red-violet powder, and it dissolves in water and alcohol very well, to form a fluorescent red solution. It dissolves in acids and bases slightly, as well as in ethanol and benzene, and its chemical formula is \( \text{(C}_{28}\text{H}_{31}\text{Cl}_{2}\text{O}_{3}) \) and its molecular weight is (479.02 gm / mole [22] when this dye dissolved in water, purity is about (99%).

Two types of polymers were used of poly vinyl pyrrolidone (PVP) & poly vinyl alcohol (PVA) polymers. (PVP, PVA) is a white powder that is attractive to moisture dissolved in water and alcohol completely freely, its chemical formula is \( \text{(C}_{x}\text{H}_{y}\text{N}_{0}) \) n as for the other polymer is a high polymer dissolved in water but it does not dissolve in acids and organic solvents it shaped white grains and its chemical formula (\( \text{C}_{2}\text{H}_{4}\text{O} \)) \( X \). This polymers are supply by (Sigma – Aldrich). The two polymers where dissolving by using the water as a Solvent,

2.2. Preparation of the samples
The preparation of samples weight prepare by using this following formula [23].

\[
W = \frac{C \times V \times M_w}{1000}
\]  

(1)

where \( W \): weight of the dye (gm), \( C \): the dye concentration (M), \( V \): the volume of the solvent (ml) and \( M_w \): Molecular weight of the solution (gm/mol).

And the different concentration can be obtained by using the following formula.

\[
C_1 \times V_1 = C_2 \times V_2
\]  

(2)

where \( C_1 \): represent high concentration (M)
\( V_1 \): represent primary volume (before dilution) (ml)
\( C_2 \): represent diluted concentration (M)
\( V_2 \): represent secondary volume (after dilution) (ml)

The absorption coefficient and refractive index have been calculated by [24][25] flowing equations:

\[
\alpha = 2.303 A/t
\]  

(3)

where \( \alpha \): absorption coefficient, \( A \): absorbence, \( t \): is the sample thickness

\[
n = \left( \frac{4R}{(1-R)^2} - K^2 \right)^{\frac{1}{2}} - \left( \frac{R+1}{R-1} \right)
\]  

(4)
where \( n \): refractive index, \( R \): reflectivity, \( K \): extinction coefficient

2.3. Measuring Instruments

UV-VIS spectrophotometer were measured by using absorption spectrum for (solution+thin films), was carried out by spectrophotometer type F96PR0 supply by (Optima, Japan, Aquarius 7000). Thin films have been prepared by using spin coating type SPIN-NXG-M1 supply by (A KISCO). For the spectroscopic study of glass samples, a spectrometer using a laser (Nd: YAG) that works on a pulse mode. Where the laser beam of wavelength (532 nm) that is pumped by a flash lamp with frequency (1Hz) passes through a pulse width (10 ns) using a lens with a focal length (10 cm) from the sample as shown in Figure 1.

![Figure 1. Laser induce fluorescence.](image)

3. Results and Discussion

The absorption spectra was measured using a UV-Visible-Spectrophotometer for dye solutions (RhB and Rh6G) with different concentrations (1x10^{-4}, 1x10^{-5} and 1x10^{-6} M) was shown in Figure 2.

![Figure 2. The absorption spectra of dyes solutions dissolved in water with a polymer (PVA, PVP) at different concentrations of dye (RhB, Rh6G).](image)
Figure 2 shows the absorption spectra of (RhB and Rh6G) dye solution doped polymer (PVA and PVP) at different concentrations of dye and the result of this absorption spectra shown in the Table 1.

Table 1. Location and maximum absorbance value of dyes (RhB, Rh6G) with polymers (PVA, PVP) at different concentrations.

| Sample                  | C(M)    | $\lambda_{\text{max}}$(nm) | A     |
|-------------------------|---------|-----------------------------|-------|
| PVA+(RhB10^{-4})        | $1 \times 10^{-4}$ | 552.599                     | 1.917 |
| PVA+(Rh6G10^{-4})       | $1 \times 10^{-5}$ | 527.359                     | 0.571 |
| PVP+(RhB10^{-5})        | $1 \times 10^{-5}$ | 550.359                     | 0.344 |
| PVP+(Rh6G10^{-4})       | $1 \times 10^{-4}$ | 525.923                     | 1.920 |

Fluorescence spectra of the solutions prepared from polymers (PVA and PVP) at concentration ($10^{-3}$ M) with (RhB, Rh6G) dyes at different concentrations ($10^{-4}$,$10^{-5}$,$10^{-6}$ M) using a fluorescence spectrometer. The results of the measurements are shown in Figure 3.

Figure 3. The fluorescence spectra with polymer (PVA and PVP) and for different concentrations of (RhB and Rh6G) dye.
Figure 3 shows that the fluorescence spectra have mixed value at \((10^{-5} \text{M})\) due to the concentration quenching and from the Table 2 is clear that the fluorescence wavelength have Blue Shift with increasing concentration.

**Table 2.** The greatest intensity of the fluorescence spectrum at its wavelength values for (RhB and Rh6G) dyes with polymer PVA and PVP for different dyes concentrations.

| Sample                | C(M)      | \(\lambda_{\text{max}}\) (nm) | A     |
|-----------------------|-----------|---------------------------------|-------|
| PVA+(RhB10^{-4})      | \(1 \times 10^{-4}\) | 590.424                         | 10.255|
| PVA+(Rh6g10^{-5})     | \(1 \times 10^{-5}\) | 555.471                         | 17.435|
| PVP+(RhB10^{-5})      | \(1 \times 10^{-5}\) | 573.027                         | 4.329 |
| PVP+(Rh6G10^{-4})     | \(1 \times 10^{-4}\) | 563.782                         | 33.953|

After obtaining the results of absorption and fluorescence, the best results of the absorption spectrum and fluorescence spectrum will be relied upon to measure the linear refractive index \((n)\) (core) and measure the refractive index of the (cladding) by entering the values of absorbance and wavelength into Equation No (4) and the measurement results were as shown in Table3.

**Figure 4.** Refractive index as a function of the wavelength of the samples chosen.

Table 3 shows the values of refractive index at the wavelengths of the samples and the result of this refractive index shown in the Table 3.
Table 3. The values of the refractive indexes at the wavelengths at which the greatest fluorescence occurred.

| Sample                  | C(M)          | \(\lambda_{\text{max}}\) (nm) | N   | n (\(\lambda = 532\text{nm}\)) |
|-------------------------|---------------|---------------------------------|-----|---------------------------------|
| PVA+(RhB\(10^{-4}\))   | \(1 \times 10^{-4}\) | 572.264                         | 2.641 | 2.600                           |
| PVA+(Rh6g\(10^{-5}\))  | \(1 \times 10^{-5}\) | 527.359                         | 2.192 | 2.150                           |
| PVP+(RhB\(10^{-5}\))   | \(1 \times 10^{-5}\) | 554.035                         | 1.886 | 1.732                           |
| PVP+(Rh6G\(10^{-4}\))  | \(1 \times 10^{-4}\) | 541.313                         | 2.642 | 2.564                           |
| PVA                     | \(1 \times 10^{-3}\) | 208.002                         | 2.839 | 1.58                            |
| PVP                     | \(1 \times 10^{-3}\) | 206.087                         | 2.980 | 1.56                            |

where four concentration glass were selected from the prepared samples depending on the best results of the absorption spectrum and fluorescence spectrum, to create a waveguide through the deposition of three layers where the first layer was a (polymer) and the middle layer was a solution (polymer doped dye) and the last layer was the same the polymer that was added to the first layer, and the results of the measurements shown in Table 4.

Figure 5. Laser induce fluorescence spectra for our samples.

A) PVA polymer doped RhB dye at concentration \(10^{-4}\) M, B) PVA polymer doped Rh6G dye at concentration \(10^{-5}\) M, C) PVP polymer doped RhB dye at concentration \(10^{-5}\) M, D) PVP polymer doped Rh6G dye at concentration \(10^{-4}\) M.
Table 4. Maximum intensity of the fluorescence spectra at the maximum wavelengths.

| Sample                  | C(M)       | \( \lambda_{\text{max}} \) (nm) | \( I(\text{max}) \) (a.u) | \( I(\lambda = 532\text{nm}) \) |
|-------------------------|------------|----------------------------------|---------------------------|----------------------------------|
| PVA+RhB \((10^4)\)+PVA | \(1 \times 10^{-4}\)       | 589.534                          | 5752.971                  | 3401.103                         |
| PVA+Rh6G \((10^5)\)+PVA| \(1 \times 10^{-5}\)       | 589.192                          | 10936.33                  | 6788.624                         |
| PVP+RhB \((10^5)\)+PVP | \(1 \times 10^{-5}\)       | 589.534                          | 4495.89                   | 3089.558                         |
| PVP+Rh6G \((10^4)\)+PVP| \(1 \times 10^{-4}\)       | 589.534                          | 8047.113                  | 4899.830                         |

From the Figure 5 it has a maximum emission at wavelength(589.534nm) and The results of the measurements are shown in Table 4. It is clear that the sample consists of PVA polymer doped RhB dye at concentration \(10^4 \text{ M}\) and the sample consist of PVA polymer doped Rh6G dye at concentration \(10^5 \text{ M}\) it have the greatest intensity fluorescence compared to the others.

Figure 6 shows absorption spectra with three concentrations \((0.1,0.06,0.02 \text{ mg / ml})\) of silver nanoparticles(Ag NPs). The nano powder of silver (Ag) have size 20 nm from US Research Nanomaterials. The sample was consist of selected from PVA polymer doped RhB dye with concentrations\((10^4 \text{ M})\) and the sample consists of PVA polymer doped Rh6G dye with concentrations\((10^5 \text{ M})\) in addition to silver nanoparticles(Ag NPs) with different concentrations.

Figure 6. The absorption spectra of silver nanoparticles(Ag NPs) at concentration (0.02,0.06,0.1mg / mL).

The absorption peak have arrived of (1.308) at wavelength (550.42nm) of PVA polymer doped RhB dye at concentration \(10^4 \text{ M}\) and arrived of (1.242) at wavelength (530.48nm) of PVA polymer doped Rh6G dye at concentration \(10^5 \text{ M}\) with different concentrations of silver nanoparticles(Ag NPs). The measurement results are as shown in Table 6, and using equations No. (1) and (2), the absorption coefficient and linear refraction were calculated as shown in Table 5.
Table 5. Value of the wavelength at the refractive index.

| Sample                  | C(AgNP) mg/mL | \(\lambda_{\text{max}}\) (nm) for \(n(\text{max})\) | \(N\) \(n(\text{max})\) |
|-------------------------|---------------|-------------------------------------------------|--------------------------|
| PVA +RhB \((10^{-4})\) | 0.02          | 535.429                                         | 2.646                    |
|                         | 0.06          | 545.029                                         | 2.642                    |
|                         | 0.1           | 550.421                                         | 2.627                    |
| PVA+Rh6G\((10^{-5})\)  | 0.02          | 530.483                                         | 2.645                    |
|                         | 0.06          | 530.483                                         | 2.647                    |
|                         | 0.1           | 530.483                                         | 2.627                    |

Fluorescence spectra of PVA polymer doped RhB dye at concentrations \((10^{-4}\text{M})\) with different concentrations of silver nanoparticles (Ag NPs).

Figure 7. Laser induced fluorescence spectra of RhB dye mixed with silver nanoparticles (Ag NPs) and at concentrations \((0.1,0.06,0.02\text{mg/ml})\).

Figure 7A shows the peak intensity of \((26979.343)\) at wavelength \((555.813\text{nm})\) at pulse energy of \((80\text{ mJ})\) for the PVA polymer doped RhB dye mixed with silver nanoparticles (Ag NPs) at concentrations \((0.1\text{mg} / \text{ml})\) compared to other energies. From the shape 6A at clear a mixture between the green and red colors due to the mixture that occurred between the exciton and the plasmon and this is called surface plasmon resonance (SPR) and the other reason is due to the different refractive indexes of waveguides leads to an increase in the total internal reflection of the middle layer (core).
it is used to increase gain. The results of the measurements of the three samples are shown in the Table 6.

**Table 6.** Value of intensity peak at the wavelength with different energy.

| Sample | pulse Energy (mJ) | C (mg/mL) | I(max)(a.u) | λ(nm) for I(max) |
|--------|-------------------|-----------|-------------|------------------|
| A      | 80                | 0.1       | 26979.343   | 555.813          |
| B      | 100               | 0.06      | 24777.872   | 555.813          |
| C      | 100               | 0.02      | 11714.204   | 555.813          |

Fluorescence spectra of PVA polymer doped Rh6G dye at concentrations (10^{-5}M) with different concentrations of silver nanoparticles (Ag NPs).

**Figure 8.** Laser induce Fluorescence spectra of Rh6G dye mixed with silver nanoparticles (Ag NPs) at concentrations (0.1,0.06,0.02mg/ml).

Figure 8A shows the peak intensity of (20357.540) at wavelength(555.015nm) at pulse energy of (100 mJ) for the PVA polymer doped Rh6G dye mixed with silver nanoparticles (Ag NPs) at concentrations (0.1mg / ml) compared to other energies. The results of the measurements of the three samples are shown in the Table 7.
Table 7. value of intensity peak at the wavelength with different energy.

| Sample | pulse Energy (mJ) | C (mg/mL) | I(max)(a.u) | λ(nm) for I(max) |
|--------|-------------------|-----------|-------------|------------------|
| A      | 100               | 0.1       | 20357.540   | 555.015          |
| B      | 100               | 0.06      | 18414.283   | 573.689          |
| C      | 100               | 0.02      | 9627.9004   | 573.689          |

4. Conclusions
By studying the absorption spectrum of polymer solutions with the dye, it is clear that the absorbance increases with increasing concentrations with a shift towards long wavelengths (Red shift). When studying the fluorescence spectrum of polymer solutions with the dye it is clear that the fluorescence increases with increasing concentrations with a shift towards short wavelengths (Blue shift). By studying the absorption spectrum of polymer film, it is clear that the PVA polymer behavior with rhodamine dyes is better than that of PVP polymer behavior with rhodamine dyes. By studying the absorption spectrum of the prepared samples, the phenomenon of surface plasmon resonance (SPR) occurs when the pulse energy (80 mJ) is applied at concentrations (0.1 mg/ml) of the silver nanoparticles (Ag NPs) and SPR effecting on threshold pumping and increase the efficiency of wave guide.

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