Molecular and fluorescence spectroscopic studies of polyacrylic acid blended with rhodamine B mixed gold nanoparticles

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ABSTRACT

This work studies the improvement of the emission spectra of polyacrylic acid (PAA) by adding different ratios of rhodamine dye (RhB) to different sizes and shapes of gold nanoparticles (AuNPs). AuNPs were prepared by chemical reduction method at heating temperature 80°C and a different time. The experimental results of both UV–Visible spectroscopy and TEM technique showed that the AuNPs were formed at different times (1–15 min) with different plasmonic band positions and has particle sizes 11 and 13 nm, for AuNPs were formed at 1 and 10 min respectively. FTIR, UV–Vis, X-ray diffraction, and SEM techniques used in the characterization of PAA blended by an equivalent amount of RhB and AuNPs with size 11 and 13 nm. The band appeared at 1683 cm\(^{-1}\) in PAA spectra which is assigned to C=O became doubling in the PAA blended samples due to the AuNPs may be coordinating with the oxygen atom in the C=O group. Fluorescence measurements indicated an emission band appeared at 585 and 590 nm for PAA doped by RhB and AuNPs with size 11 and 13 nm, respectively. The intensity of these emission bands was enhanced for the PAA blended by increasing both AuNPs and RhB ratios due to the interactions between dipole moments of the SPR of the AuNPs and RhB molecules. Therefore, it could be enhancing the fluorescence intensity of these samples, and it can be used as a laser active medium.

Highlights

- Synthesis of AuNPs with different sizes.
- Prepare PAA blended by RhB and AuNPs.
- Study the coordination of AuNPs with PAA using FTIR.
- Explain the effect of RhB and AuNPs on fluorescence spectra.

ARTICLE HISTORY

Received 15 March 2020
Revised 15 May 2020
Accepted 19 May 2020

KEYWORDS

Gold nanoparticles; dye doped polymer; FTIR; fluorescence

1. Introduction

Noble metal nanoparticles have a particular position in the scientific community for their different optical properties, high surface to volume ratio, and surface plasmon resonance (SPR) [1]. SPR is a resonance obtained between the incident wavelengths and the collective oscillation of electron in the conduction band in the surface of metal nanoparticles (MNs), which is smaller than the incident light wavelength [2]. AuNPs have promising applications because of their physical, chemical, and fluorescent properties. These characteristics make it unanticipated applications in magnetic, electronics, and optical devices. Gold nanoparticles have received considerable attention from scientists because they are more stable and more application. Physical and chemical methods have been developed, some of which have been refined recently to fabricate metal nanostructures [3]. In the chemical method of metal NPs preparation, almost the synthesis parameters affect the size and shape, although the exact mechanisms involved in the size tuneability of noble metal NPs are still uncertain [4]. On the other hand, noble metal NPs were also synthesized using biological extracts due to cost-effective and scalable [5,6]. Different methods of synthesizing AuNPs by reduction of Au\(^{3+}\) ions using chemical reducing agents in solution have been reported [7]. Gold nanoparticles can be synthesized in various forms, including nanoshells, nanospheres, nanoprisms, and nanorods for a wide variety of applications. Murphy group [8] and Bastús et al. [9] prepared monodispersed gold nanoparticles in different size ranges (5–200 nm) diameter through reduction technique and controlled seeded growth through different reaction conditions as a solvent, reducing and stabilizing agent. Fluorescence occurs when the incident light excites the molecules; this makes molecules emit the light with the
wavelength larger than incident wavelength [10]. The fluorescence of MNs could enhance the fluorescence of fluorophores when embedded dye with MNs, owing to the interactions among the dipole moments of the SPR of the MNs and the fluorophores of dye molecules [11]. Metal nanoparticles doped by polymers have been exploited for broad and different fields due to electrical and optical properties that depend on doped materials. Among several of these polymers, polyacrylic acid [12]. Moreover, polymers have an essential role in the metal nanoparticles doped by the dye, its works as a capping agent, in order to prevent the agglomerated of MNs during preparation [13]. Rhodamine B was used as a dye due to its fluorescent, it has photophysical properties, and excellent photo-stability [14].

In this work, we try to improve the fluorescence emission spectra of the polyacrylic acid blended by RhB (dye) and AuNPs with different sizes and shapes. Also, it is to understand how the addition of RhB and AuNPs in polyacrylic acid is effective in enhancing the fluorescence, due to the energy transfer from the fluorophores to the AuNPs.

2. Materials and methods

2.1. Materials

Gold (III) chloride hydrate H(AuCl4)_3H2O was purchased from Electron Microscopy Science (Hatfield, PA). Trisodium citrate (TSC) C3H5Na3O7.2H2O was purchased from Sigma-Aldrich (USA). Polyacrylic Acid [C3H4O2] with a molecular weight of 450,000 g/mol, was purchased from Sigma-Aldrich (USA). Rhodamine B (C28H31ClN2O3) dye content ≥ 95%, was purchased from ACROS (USA).

2.2. Preparation of AuNPs

Gold salt was dissolved in distilled water with a molar ratio of (1 × 10⁻⁴ M) as a stock solution. Trisodium citrate in concentrations of 1% was dissolved in distilled water. Gold nanoparticles were formed by preparing 11.31 ml of HAu Cl₄ (3H₂O) with a molar ratio of (5.5 × 10⁻³ M) and was added to 588.66 ml distilled water and heated under magnetic stirring, after 20 s of heating at 80°C. 0.0528 g of trisodium citrate was added to get concentrations of (3.24 × 10⁻⁴ M) of TSC in a mixture. The colour of the solution was changed to red. Just as the colour changed, we pulled 75 ml of the mixture at 0, 1, 2, 3, 5, 7, 10, and 15 min, respectively.

2.3. Fabrication of PAA blended by RhB and AuNPs thin Films

Eight grams of PAA (450,000 g/mol) was added to 200 ml distilled water under magnetic stirring. The solution was heated until completely dissolved, at which 5 ml of dissolved PAA was poured on a petri dish (9 cm) to form a thin film. Rhodamine B (RhB) 0.074901 g was dissolved in 100 ml of distilled water under magnetic stirring at room temperature. To get an excellent thin film from PAA blended by RhB and AuNPs, 5 ml of dissolved PAA mixed with different ratios have an equivalent amount of RhB (5 × 10⁻⁵ M) and AuNPs that prepared at 1 and 10 min and poured on a petri dish, respectively.

2.4. Samples characterization

The surface plasmon resonance of AuNPs colloidal was carried out using the UV–VIS–NIR spectrometer (Thermo-scientific Evolution 220 Spectrophotometer) at a resolution of 2 nm. Transmission electron microscope (TEM) was used to analyse sample morphology and to calculate the particle sizes. To prepare the samples for measuring:10 ml of the sample solution was placed on carbon-coated 200 mesh copper grids and allowed to air dry. TEM of the samples was performed using a JEOL JEM-1100 microscope (JEOL Ltd., Tokyo, Japan) equipped with a tungsten thermionic gun operating at a 100-kV accelerating voltage. TEM images were acquired by a CCD camera. The vibrational spectra were carried out using Jasco Model 300E Fourier Transform Infrared Spectrometer. The X-ray diffraction pattern was measured using CuKα radiation at 40 kV and 40 mA, and λ of 1.5406 Å. The scanning was performed over 2θ range from 30° to 90° at a speed of 0.02°/s. The crystal size of the nanoparticles was calculated using Scherrer’s formula. Morphological characterization was carried out by using scanning electron microscopy (JSM-6380 LA). The fluorescence spectra were measured using the Jasco FP777 spectrophotometer. The light source is xenon arc lamp 150 W.

3. Results and discussion

3.1. Ultraviolet–Visible spectra of AuNPs

The size and distribution of the nanoparticles can be comparable to the position and half-bandwidths of the surface plasmon resonance (SPR) band [15,16]. Figure 1 shows the UV–VIS spectra of AuNPs prepared at T = 80°C for different times. From this figure, absorption peaks were observed at different wavelengths in the range 516–540 nm for the samples prepared for 1, 2, 3, 5, 7, 10, and 15 min after the colour change to brown-red. These bands are attributed to surface plasmon resonance (SPR) bands. An SPR band is defined as a resonance influence generated a result of the interaction between the incident photons and electrons on the surface of AuNPs. Based on the work reported by Jayasmita [17], the localized surface plasmon resonance (LSPR) manifested because of the collective coherent
electron oscillation at the surface of the Au nanoparticle, and an electric field was generated around the nanoparticle due to the photon interactions. The interaction between the incident photon and nanoparticles depends on their size and shape, as well as on the dielectric of the dispersion medium [18]. The surface plasmonic band was selected as a means of studying the optical applications of metal nanoparticles at visible wavelengths. As Figure 1 shows, the position of absorption band was 540, 530, 538, 528, 529, 525, 522 and 516 nm for the samples prepared for 1, 2, 3, 5, 7, 10, and 15 min, respectively. These spectra are dependent on preparation time and the size of AuNPs. The SPR bands changed to lower wavelengths with an increase in duration of heating at 80°C, as shown in Figure 2. The change to lower wavelengths (higher energy), known as a blue shift, indicates a decrease in the particle sizes of AuNPs [17]. In addition, the curvature of the nanoparticles can be affected by the SPR, such that at a very low surface curvature (a small particle size). The surface plasmon band shifted to lower wavelength and became narrower due to the orbitals being slightly farther from each other, resulting in a high energy resonance. Therefore, the blue shift was observed for small particle sizes. With the higher curvature in case of larger particle size, SPR shifted to higher wavelengths (a red shift), and surface plasmon bands became wider owing to the orbitals overlapping to a greater extent. Moreover, it was found that the half-bandwidth decreased with the decrease in particle size. The distribution of nanoparticles in solution reflects the number density. This number may be more affected than the volume fractions in cases of quantum size effect [19]. The particle size decrease with increasing heating times is probably due to the acceleration of the formation of Au$^+$ and the breaking of the bonds of the surface nanoparticles, which reduces the size of AuNPs. In other words, the increase in the heating time may increase the chemical reduction between tri-sodium citrate and Au$^+$ nanoparticles, which thickens the tri-sodium citrate shell and reduces the cores of AuNPs. Colour intensity and absorbance rates increased over the reaction time, suggesting an increase in the number of AuNPs and indicating a continuous reduction in gold ions. These results are consistent with a previous study by Ramakrishna [19].

3.2. TEM of AuNPs prepared at 80°C for different times

Figure 3(a) shows the TEM image of AuNPs prepared at $T = 80°C$ for 1 min, that mean the sample was taken in the first minute of AuNPs formation in solution. It can be seen that the gold nanoparticles have been observed and confirmed as black spot size, generally are spherical in shape, but sometimes are pyramid-, cylinder- or character-L-shaped as well. Particle sizes have been determined by measuring the diameter of all spherical nanoparticles on TEM images and found to be around $\sim 11$ nm. From the TEM image of AuNPs prepared at $T = 80°C$ for 10 min, Figure 3(b) that mean the sample was taken in the tenth minutes of AuNPs formation in solution, it can be seen that the gold nanoparticle appears as a dark point with a spherical shape. The average size of the particle was estimated and found to be $\sim 13$ nm.

3.3. FTIR spectroscopy of RhB, PAA, and PAA blended by RhB and AuNPs (with size $\sim 11$ and $\sim 13$ nm)

Figure 4(a) shows the transmittance spectrum of RhB. The band appeared at 3420 cm$^{-1}$ is interpreted as the vibrations of the hydroxide group as a result of the sample’s absorption of water molecules. The bands appear at 2960, and 2820 cm$^{-1}$ are assigned to the symmetric and asymmetric stretching vibrations of CH bond.
in the CH$_3$ group. The two bands that are clearly visible at 1690 and 1640 cm$^{-1}$ are explained as the C=O and C=C stretching vibrations respectively. The bands that appear in the 1578–1466 cm$^{-1}$ range are characteristic aromatic ring vibrations. The band observed at 1405 cm$^{-1}$ indicates the bending vibration of C–H bond in the group =N+(C$_2$H$_6$), while the C–N-linked benzene ring is indicated by the appearance of the band at 1336 cm$^{-1}$. The band set at about 1246 cm$^{-1}$ is assigned to the stretching vibration of C–O–C and the band at 1070 cm$^{-1}$ is a result of stretching vibration of C–O–H. The band at 1005 cm$^{-1}$ corresponds to the C–O stretching vibration. The emergence of transmittance bands at 920 cm$^{-1}$ is attributed to the bending vibration of O–H in carboxylic acids. The two bands located at 780 and 681 cm$^{-1}$ are attributed to the C–H bending vibration, as is the band shown at 576 cm$^{-1}$, which is assigned to C–H out-of-plan bending vibration in the aromatic ring. The band that appears at 498 cm$^{-1}$ is assigned to C=C–C [20]. Figure 4(b) shows the infrared spectrum of poly (acrylic acid) in the wavenumber range of 4000–400 cm$^{-1}$. The observed peaks in the 3700–3000 cm$^{-1}$ range are suggested to
It was shown that the absorption band appearing at 3424 cm\(^{-1}\) may be characteristic of the ratio of PAA blended with two different molar ratios as cleared in Figure 4(d). This band is assigned to the C–O group, and RhB may be responsible for this shift. The absorbance band at 3461, 3477, 3470, and 3473 cm\(^{-1}\) in Rh:AuNPs ratios (0.5:0.5), (1:1), (2:2), and (3:3), respectively. This is because the change in PAA structure resulting from the addition of AuNPs and RhB. The band at 3349 cm\(^{-1}\) was shifted to a higher wavenumber at (3373 and 3363 cm\(^{-1}\) in samples Rh:AuNPs ratios (0.5:0.5) and (1.5:1.5), and to a lower wavenumber (3266 and 3330 cm\(^{-1}\) in samples Rh:AuNPs ratios (2:2) and (3:3), respectively. The band appearing at 3212 cm\(^{-1}\) in PAA moved to a higher wavenumber (3247 and 3241 cm\(^{-1}\) in samples Rh:AuNPs ratios (1:1) and (1.5:1.5), and shifted to a lower wavenumber (3191, 3203, and 3166 cm\(^{-1}\) in samples Rh:AuNPs ratios (0.5:0.5), (2:2) and (3:3), respectively. This may be owing to the electrostatic interaction of AuNPs with CO–OH in blended PAA. The band appearing at 2944 cm\(^{-1}\) in PAA was changed to a lower wavenumber as a result of adding CH in RhB. The band at 1683 cm\(^{-1}\) is splaying and moved to a lower wavenumber, in my view because the AuNPs affected the electronegativity of the C–O group in the PAA. The band at 1243 cm\(^{-1}\) become broad and new band at 1220 cm\(^{-1}\) was observed. The band at 1197 cm\(^{-1}\) combined with 1243 cm\(^{-1}\) due to the change of structure during the addition of RhB and nanoparticles. This is possible on account of the electrostatic interaction between AuNPs and the oxygen atom in C–O. All these bands and their assignments were summarized in Table 1.

### 3.4. UV–Visible spectra of PAA blended by RhB and AuNPs (11 and 13 nm)

The polycrylic acid film is transparent and has no absorption band in the wavelengths of the visible range. Figure 5(a) shows the absorption spectra of PAA film blended with an equivalent amount of RhB and AuNPs size (11 nm) and different molar ratios. It is known the AuNPs has an absorption band in the 540–516 nm range, and RhB has a band at 552 nm. Comparing PAA spectrum and PAA doping one, it was found that a new band appeared in the PAA doping at 560 nm and a shoulder at about 525 nm. This band and shoulder were assigned to the π−π* transition of RhB and surface plasmon band of AuNPs, respectively. The absorption band of RhB, formerly at 552 nm, was moved to the higher wavelength at 560 nm, and the surface plasmon band turned into the shoulder at 525 nm. This is perhaps due to the plasmon band overlapped with the RhB band so that the RhB band became broad and shifted to a higher wavelength. Likely, the interaction between trisodium citrate (capping of AuNPs) with RhB was responsible for this shift. The absorbance band intensity at 560 nm was increased with increases in the molar ratios of both AuNPs and RhB, and this increase follows the Beer–Lambert Law.

On the other hand, it observed that the half-bandwidth of π−π* at 560 nm decreases, and the absorption intensity increases at higher ratios of AuNPs and RhB. This increase is due to the increase in the colour intensity of the PAA film. Figure 5(b) shows the absorption spectra of PAA embedded with an equivalent amount of RhB and AuNPs (13 nm) with different...
be concluded that the RhB does not affect the AuNPs that occurred during the embedding AuNPs in molar ratios. The absorption band that appeared in the spectra at 563 nm, and the shoulder at 526 nm, were linked to RhB and AuNPs, respectively. By increased RhB and AuNPs, the intensity of the band at 563 nm and the shoulder at 526 nm, were increased with ratios. The absorption band that appeared in the spectra at 563 nm, and the shoulder at 526 nm, were linked to RhB and AuNPs, respectively. The diffraction pattern was similar to the Bragg’s reflection of AuNPs. These results agreed with the data in JCPDS card no. 89-3697. These peaks confirm that the AuNPs exist as natural crystals. It can, therefore, be concluded that the RhB does not affect the AuNPs structures [22]. The crystal sizes (D) were estimated at each peak using Scherrer’s formula [20],

\[ D = \frac{k\lambda}{\beta \cos \theta^\circ} \]

where k is constant dependent of crystals shape (0.9), \( \theta^\circ \) is the Bragg angle, \( \beta \) is the full width half maximum (FWHM) in radians of the X-ray peak and \( \lambda \) is the X-ray wavelength (0.1540562 nm). The estimated values of the crystal size were found to be 25, 22, 21, 25, and 18 nm, for the peaks at 2\( \theta^\circ \) = 37.39°, 43.62°, 64.5°, 76.95° and 81.16°, and: 27, 25, 26, 26, and 19 nm for the peaks that appeared at 2\( \theta^\circ \) = 37.4°, 43.6°, 63.91°, 77.0°, and 81.18° at PAA blended by RhB and AuNPs (11 and 13 nm), respectively. The average crystal size calculated for all these peaks of the two samples at (24 and 26 nm). The calculated crystal size was then compared with particle sizes measured from TEM images. It is worth noting that, the value of the nanoparticles calculated from the X-ray was greater than that of the particles found by TEM. This may be due to some agglomeration of AuNPs that occurred during the embedding AuNPs in

| Band Positions |
|----------------|
| RHB | PAA | PAA/Rhb/AuNPs 11 nm | PAA/Rhb/AuNPs 13 nm | Assignment |
| 3420 cm\(^{-1}\) | 3700–3000 cm\(^{-1}\) | 3700–3000 cm\(^{-1}\) | 3700–3000 cm\(^{-1}\) | \( \nu_1 \) and \( \nu_{3u} \) of the (OH) in water |
| 2960 cm\(^{-1}\) | 2944 cm\(^{-1}\) | 2960 cm\(^{-1}\) | 2964 cm\(^{-1}\) | \( \nu_1 \) and \( \nu_{3u} \) of the (CH) of the CH\(_3\) group |
| 2910 cm\(^{-1}\) | - | 2944 cm\(^{-1}\) | 2904 cm\(^{-1}\) | |
| 2820 cm\(^{-1}\) | - | 2854 cm\(^{-1}\) | 2854 cm\(^{-1}\) | |
| - | ~ 2645 cm\(^{-1}\) | 2645 cm\(^{-1}\) | 2645 cm\(^{-1}\) | Overtone and combination of the (C–O) and (C–H) groups |
| 2225 cm\(^{-1}\) | - | 1712 cm\(^{-1}\) | 1712 cm\(^{-1}\) | \( \nu_1 \) of (C = O) |
| 1690 cm\(^{-1}\) | 1683 cm\(^{-1}\) | 1683 cm\(^{-1}\) | 1683 cm\(^{-1}\) | \( \nu_1 \) of (C = O) |
| 1578 cm\(^{-1}\) | - | 1619 cm\(^{-1}\) | 1619 cm\(^{-1}\) | (C = O) \( \nu_3 \) |
| 1466 cm\(^{-1}\) | - | - | - | Aromatic ring vibrations |
| 1436 cm\(^{-1}\) | 1436 cm\(^{-1}\) | 1436 cm\(^{-1}\) | 1436 cm\(^{-1}\) | \( \delta \) of (C–O–H) belonging to pendant group of (COOH) |
| 1405 cm\(^{-1}\) | - | - | - | |
| 1336 cm\(^{-1}\) | - | - | - | |
| 1246 cm\(^{-1}\) | - | 1297 cm\(^{-1}\) | 1243 cm\(^{-1}\) | (C–O) coupled with (O–H) in plane bending vibration |
| 1197 cm\(^{-1}\) | 1182 cm\(^{-1}\) | 1197 cm\(^{-1}\) | 1197 cm\(^{-1}\) | (C–O–H) group. |
| 1173 cm\(^{-1}\) | - | - | - | \( \nu_1 \) of (C–O–C) |
| 1070 cm\(^{-1}\) | - | 1045 cm\(^{-1}\) | 1045 cm\(^{-1}\) | \( \nu_1 \) of (C–O–H). |
| 1005 cm\(^{-1}\) | 919 cm\(^{-1}\) | 919 cm\(^{-1}\) | 919 cm\(^{-1}\) | CH\(_3\) rock. |
| 920 cm\(^{-1}\) | 919 cm\(^{-1}\) | 919 cm\(^{-1}\) | 919 cm\(^{-1}\) | \( \nu_1 \) of (C–O) |
| 780 cm\(^{-1}\) | 802 cm\(^{-1}\) | 802 cm\(^{-1}\) | 802 cm\(^{-1}\) | \( \delta \) of (C–H) carboxylic acids |
| 681 cm\(^{-1}\) | - | 634 cm\(^{-1}\) | 634 cm\(^{-1}\) | \( \nu_1 \) of (C–COOH) group. |
| 576 cm\(^{-1}\) | - | 634 cm\(^{-1}\) | 615 cm\(^{-1}\) | \( \delta \) of (C–H) |
| 490 cm\(^{-1}\) | - | - | - | (C–H) out of plane bending vibration in the aromatic ring |

\( \nu = \) stretching vibration, \( \nu_1 = \) symmetric stretching vibration, \( \nu_{3u} = \) antisymmetric stretching vibration, \( \delta = \) bending vibration.

3.5. X-ray diffraction of PAA blended with equivalent amounts of RhB and AuNPs sizes (11 and 13 nm)

Figure 6 shows the change in the X-ray diffraction pattern intensity with 2\( \theta^\circ \) in the 30° to 85° range of PAA blended with an equivalent amount of RhB and AuNPs of sizes (11 and 13 nm). From this figure, one can see that the diffraction peaks that appeared at 37.39°, 43.62°, 64.5°, 76.95° and 81.16° have different intensities and matched with the planes 111, 200, 220, 311 and 222, respectively. The X-ray diffraction pattern was similar to the Bragg’s reflection of AuNPs. These results agreed with the data in JCPDS card no. 89-3697. These peaks confirm that the AuNPs exist as natural crystals. It can, therefore, be concluded that the RhB does not affect the AuNPs structures [22]. The crystal sizes (D) were estimated at each peak using Scherrer’s formula [20],

\[ D = \frac{k\lambda}{\beta \cos \theta^\circ} \]
Figure 5. Absorption spectra of (a) PAA film doped by an equivalent amount of RhB and AuNPs (11 nm) with different molar ratio, and (b) PAA film doped by an equivalent amount of RhB and AuNPs (13 nm) with different molar ratio.

3.6. SEM of PAA blended by an equivalent amount of RhB and AuNPs (11 and 13 nm)

Figure 7(a, b) shows a scanning electron microscope (SEM) images of PAA blended with equivalent amounts of RhB and AuNPs (11 and 13 nm). From these two images, it can be noted that the nanoparticles appear as white spots with spherical or prism-like shapes. In scope, they appear in a random distribution with different sizes and shapes (see Figure 7(a)). It can be concluded that the gold nanoparticles of size (11 nm) mixed with RhB at the same molar ratio are randomly distributed in PAA film, and also of irregular size. They, too, appear as white spots with different shapes, as indicated in Figure 7(b).

3.7. Fluorescence spectra of PAA film blended with equivalent amounts of RhB and AuNPs (11 and 13 nm) with different molar ratios

Figure 8(a, b) shows the fluorescence spectra of a transparent polymer (PAA) blended with two equivalent amounts of RhB and AuNPs of size (11 and 13 nm) at the different molar ratio in the 380–680 nm range. Here, the samples were excited at the absorption wavelength of the surface plasmon band of AuNPs, overlapping with the absorption band of RhB, which measured at 560 nm in our previous UV–VIS results. From Figure 8(a), one can see that the emitted bands are cleared at 585, 585.5, 585.5, 588, and 589.5 nm, as well as at 420, 422, 418, 418.5, 420.5, and 422 nm for the samples with the RhB:AuNPs (with size 11 nm) and with composite in ratio (0.5:0.5), (1:1), (1.5:1.5), (2:2), (2.5:2.5), and (3:3), respectively. As indicated in this figure, the lower-wavelength fluorescence bands for RhB are due to the absorbance band at 350 nm. The fluorescence intensity bands appeared at about 585 nm increased with the increase in the ratio of RhB and AuNPs, as shown in the inset figure. The fluorescence intensity bands that appeared at about 420 nm were weak compared to the fluorescence intensity bands observed at about 585 nm. This is maybe due to the weak excitation at the lower wavelengths. The emitted energy is less than the exciting energy, which may be owing to some
loss of energy through heat or vibration in the excited molecules. The position of the emitted fluorescence depended on the difference in the dipole moments between the ground state (S0) and the first excited state (S1) of the RhB molecules. It can be noted that a red-shift in wavelength, from 585 to 585.5 nm, from 585.5 to 588 nm, and from 588 to 589.5 nm, was observed from the lowest to the highest concentration of samples. A small linear increase was observed in the emission wavelength with an increased molar ratio of AuNPs and RhB due to the colour-bearing groups [1]. The observed peak and shoulder for the highest concentration of PAA blended with RhB and AuNPs occurred at longer wavelengths due to the existence of intermolecular interactions in the ground state in the PAA films and its doping. One of the most significant characteristics of the RhB and AuNPs-blended film is indicated by the Stokes shift formula, which describes the difference in the dipole moments between the ground state (S0) and the first excited state (S1) of the dye molecules. A measure of self-absorption of the fluorescent emitted rays can be calculated using the following relation [23].

\[ \nabla \lambda = \lambda_f - \lambda_a \]  

where \( \lambda_f \) and \( \lambda_a \) are the wavelengths of the fluorescence and the absorbance maxima, respectively. The spectral features of the lasing RhB and AuNPs-blended polymer depend on the intermolecular interaction between the RhB molecule and AuNPs with the macromolecules [11, 24–26]. In the presented study, it was found that the spectra of the blended polymer depend on the intermolecular interaction between AuNPs, RhB, and PAA. In addition, the Stokes shift values, as represented in Table 2, were increased by increasing the molar ratio of AuNPs and RhB, which indicates a low self-absorption of the fluorescent light emitted through the AuNPs and RhB molecules.

From Figure 8(b) two fluorescence bands appeared: one at 582, 584, 585, 590, 590, and 588.5 nm, and the other at 402.5, 404.5, 410.5, 408.5, 409, and 405.5 nm. These emitted bands referred to RhB absorbance bands at 350 nm, for the samples with the RhB:AuNPs (11 nm) is (0.5:0.5), (1:1), (1.5:1.5), (2:2), (2.5:2.5), and (3:3), respectively. The fluorescence intensity spectra increased with an increase in the ratio of RhB and AuNPs, as shown in inset Figure 8(b). The fluorescence intensity bands that appeared at about 404 nm were weak compared to the fluorescence seen at about 590 nm. This is because
Table 2. Photophysical properties of PAA film blended with equivalent amounts of RhB and AuNPs (11 and 13 nm) with different molar ratios.

| RhB: AuNPs | 0.5:0.5 | 1.0:1.0 | 1.5:1.5 | 2.0:2.0 | 2.5:2.5 | 3.0:3.0 |
|-----------|---------|---------|---------|---------|---------|---------|
| Absorption wavelength (λ\_a) | 580.5 nm | 585.0 nm | 585.5 nm | 585.5 nm | 588.0 nm | 589.5 nm |
| Fluorescence wavelength (λ\_f) | 582.0 nm | 584.5 nm | 585.0 nm | 590.0 nm | 590.0 nm | 588.5 nm |
| ∆λ = λ\_f − λ\_a | 20.5 nm | 25.0 nm | 25.5 nm | 25.5 nm | 28.0 nm | 29.5 nm |

4. Conclusion

The results of TEM confirmed the formation of AuNPs with various sizes and shapes, and the effect of preparation time on surface plasmon resonance (SPR) was clarified. FTIR results showed the bands appeared at 1683 and 1243 cm\(^{-1}\), which were shifted after doping PAA with different molar ratios of RhB to PAA. It can be inferred that gold nanoparticles and RhB blended in PAA film enhanced their fluorescence spectra of these samples. These means that these samples emit fluorescence with enhancing intensity and can be used as a dye laser medium.

Disclosure statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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