



EFFECT OF SILVER NANOPARTICLES ON FLUORESCENCE INTENSITY OF R610 DYE WHICH THEY INCORPORATE INTO SOL-GEL HOST

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ABSTRACT

This work aim to study the effect of silver nanoparticles on fluorescence intensity of R610 dye, Silver nanoparticles which is prepared by using the chemical reduction method, AgNP colloidal 5 and 10 min as a reduction periods mixed with R610 dye solution and incorporating this mixture into sol-gel host. The optical properties of prepared samples are tested by using UV-VIS absorption spectrophotometer and Fluorescence spectrophotometer.

KEYWORDS: silver nanoparticles, AgNP, UV-VIS, Fluorescence spectrophotometer.

INTRODUCTION

The sol-gel process is a convenient and versatile method of preparing transparent optical materials at low temperature^[1]. Sol-gel synthesis is a complex chemical reaction involving the presence of various intermediates during the synthesis process^[2]. The caging of nanoparticles within the gels is very important for a number of technological applications. A homogeneous distribution of the particles within the gel must be obtained, which control both monodispersity and particle size^[3]. Metallic silver colloids were first prepared more than a century ago. Ag nanoparticles can be synthesized using various methods; the most popular preparation of Ag colloids is chemical reduction of silver salts by sodium citrate^[4]. The reason for the unique spectral response of Ag nanoparticles is that special wavelengths of light can derive the conduction electrons in the metal to collectively oscillate. This oscillation is known as surface plasmons resonance (SPR). It causes the absorption and scattering intensities of nanoparticles^[5]. The presence of nearby metallic surfaces or particles can alter the free-space condition of fluorophore and can result in dramatic spectral changes^[6]. Metal-enhanced fluorescence (MEF) is a promising technique which utilizes the positive effect of metal nanoparticles on the fluorescence signal of fluorophore in order to increase the sensitivity of traditional fluorescence techniques, and it is attributed to a coupling of dye with an electromagnetic (EM) field near the metal particle. The EM field is regarded to be dependent on the features of the metal particle (metal species, size, shape, *etc.*)^[7]. The general solution of the interaction problem between a single homogeneous sphere, of radius R, and of arbitrary material with an incident electromagnetic field was first given by G. Mie in 1908^[8]. Mie's calculations give a series of multipole oscillations for the absorption and the scattering cross section of the particles as a function of the particle radius. The extinction spectrum is then composed of the sum of absorption and scattering modes, each of which has a contribution that depends on the particle size.

Higher-order modes become more dominant with increasing particle size^[9]. Whereas the scattering varies with the average radius of the particle, index of refraction, scatter density and the incident wavelength. If the particle size is small compared to the wavelength, scattering (in all directions) occurs. Whereas, bigger particles reflect and refract light^[10]. If there are many scatterers randomly distributed inside the medium, the incident light wave will undergo scattering and the scattered light will have a random path^[11]. On the occurrence of multiple scattering, the time period in which the light stays in the amplification medium increases (light energy density increases) which affects the spectral properties of emission. Multiple random scattering provides the mechanism of optical feedback.

EXPERIMENTAL WORK

Materials

Silver nitrates AgNO₃, sodium citrate Na₃C₆H₅O₇ were received from Sigma Aldrich, Tetraethoxysilane TEOS from Sigma Aldrich, R610 dye these materials had been used without further purification.

Preparation of silver nanoparticles

0.0425 gm of AgNO₃ dissolved in 50mL deionized water to prepared 50 ml as a starting solution of $\sim 5.0 \times 10^{-3}$ M of AgNO₃ in water, in order to reach 10^{-3} M concentration, 25mL of AgNO₃ solution was added to 100mL of H₂O (now $\sim 1.0 \times 10^{-3}$ M). In another hand a solution of 1% sodium citrate (0.5 gm in 50mL of H₂O) has been prepared, and then the 125mL solution of AgNO₃ was heated until it begins to boil at 97 °C. At a moment of boiling 5mL of 1% sodium citrate solution has been added drop by drop, as soon as boiling commences colloidal solution color is gradually changed from light yellow to dark brown that's an indication to silver nanoparticles creation. Where yellow color of the solution is indicate to small particle size while dark brown is indicate to bigger particles size.



FIGURE 1: prepared silver Nanoparticles by a hot chemical reduction method with 5 and 10 min reduction periods

Incorporation of the AgNP and Dye mixture into sol-gel matrices

Firstly, two solutions, silica solution containing TEOS and pure ethanol were mixed in a volume ratio of 1:2 and denoted as sol (A). In another container, a catalyst solution containing deionized water mixed with catalyst, HCl, mixed with pure ethanol at volume ratio 2:1:1 denoted as sol (B) then mixture of AgNP and R610 dye was added to sol (B). The sol (B) was slowly added to sol (A) with

magnetic stirring for one hour to ensure homogeneity, then 0.5ml of N-N dimethylformamide was added as drying control chemical additive (DCCA) to the final sol, that all illustrated in Figure 2. The final sol was poured in sealed glass tube and was left in oven 70°C. The aging process was achieved after reaching the gel point after seven days. Then shrinkage started until the rod had a final shape after 15 days (Figure 3), absorption and fluorescence spectra have been getting to it.

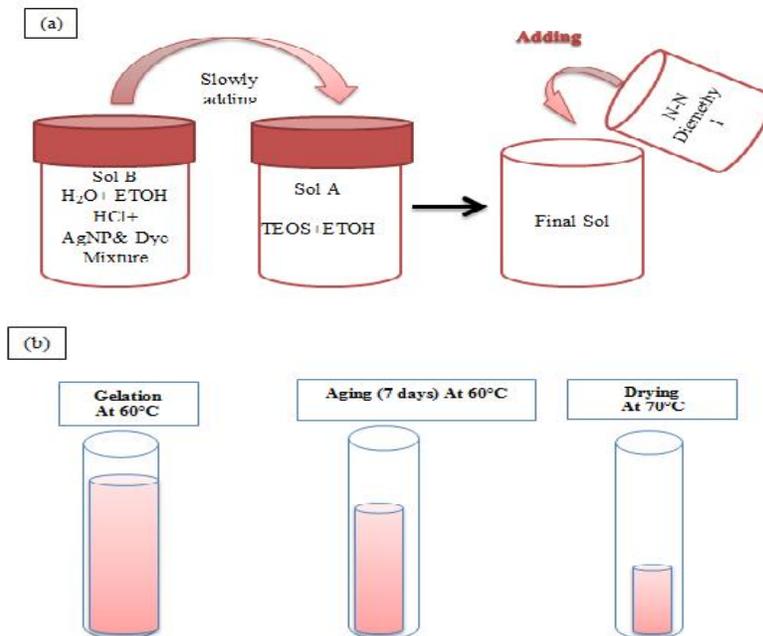


FIGURE 2: Overall Sol-gel synthesis (a) mixing process, (b) The aging process



FIGURE 3: Final form of R610 dye of Sol-gel rods

Absorption & Fluorescence Spectra of AgNP & a dye in sol-gel rod

a. Absorption spectra of AgNP&R610 in sol-gel rod

The absorption spectra of a rod shape R610 dye mixed with AgNP colloidal (5 minutes) and (10 minutes) which incorporated into the silica matrix represented in Figure 3 and Figure 4. By looking for these Figures it can be

noticed an increasing in the absorption intensity of R610 when AgNP colloid added to it, at the case of (5 min) as a reduction period of AgNP, the maximum peak absorption intensity was gated at adding 40% of AgNP colloid, while the maximum absorption intensity in case of (10 min) as a reduction period of AgNP occurred at adding 10% of AgNP colloid to R610 dye solution.

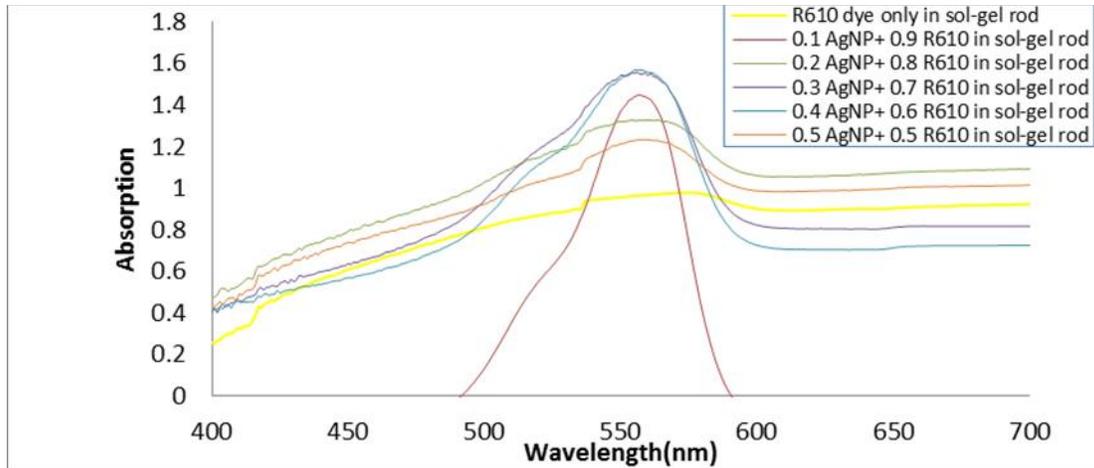


FIGURE 3: the absorption intensity of AgNP (5 minutes) & R610 dye mixture in sol-gel rod

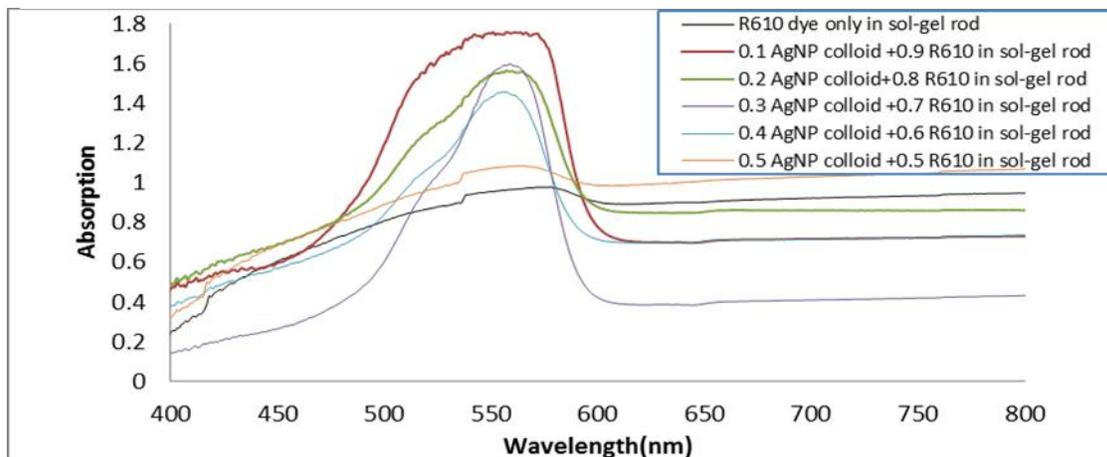


FIGURE 4: the absorption intensity of AgNP (10 minutes) & R610 dye mixture in sol-gel rod

b. Fluorescence spectra of AgNP&R610 in sol-gel rod

The fluorescence spectra of R610 and (5 min) AgNP described in figure 5 below. From this Figure and table 1 one can note increase the fluorescence intensity of R610 dye that's mixed with (5 min) AgNP as a reduction period and incorporates into sol-gel rod, the maximum peak position of fluorescence spectra of R610 dye only in sol-gel rod was at 608 nm, by adding a different ratio of AgNP (10%-50%) to it, one can notice a significant shifting of the peak positions toward short wavelengths (blue shift)

until it reach to 598nm. The fluorescence intensity of R610 dye in sol-gel rods has been increased, by increasing the mixing ratio until it reached to a maximum value at 50% as a mixing ratio of AgNP colloid with enhancement factor 2.51 as illustrated in Figure 5. Figure 6 where it shows the gradual increase of maximum fluorescence intensity of the dye as a function to mixing ratio. Figure 7 shows that FWHM very little decreased by increasing the maximum fluorescence (this accepted behavior), it's back to increase at maximum fluorescence value (50% AgNP).

Silver nanoparticles on fluorescence intensity of R610 dye

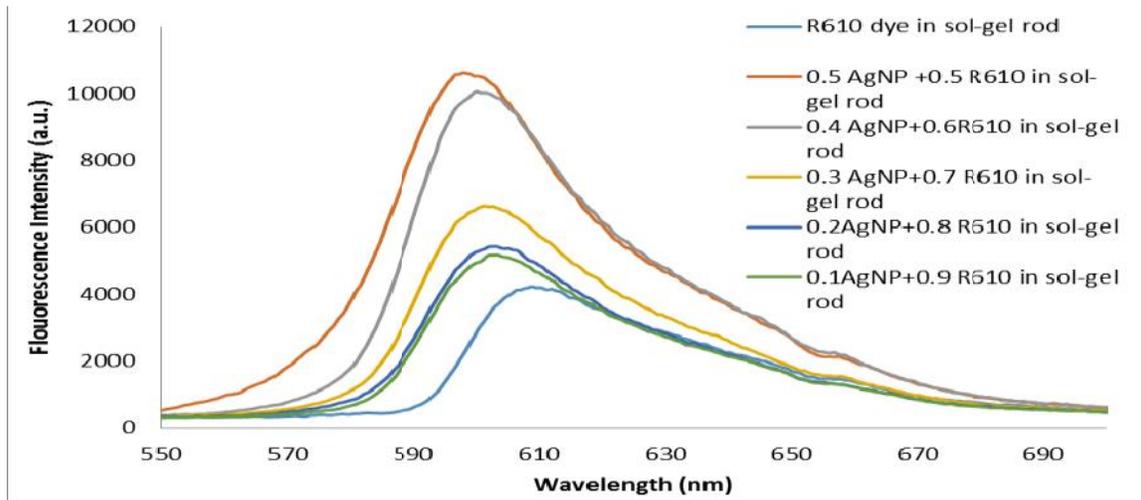


FIGURE 5: total fluorescence of AgNP(5 min) and R610 mixture in sol-gel rod at different mixing ratio

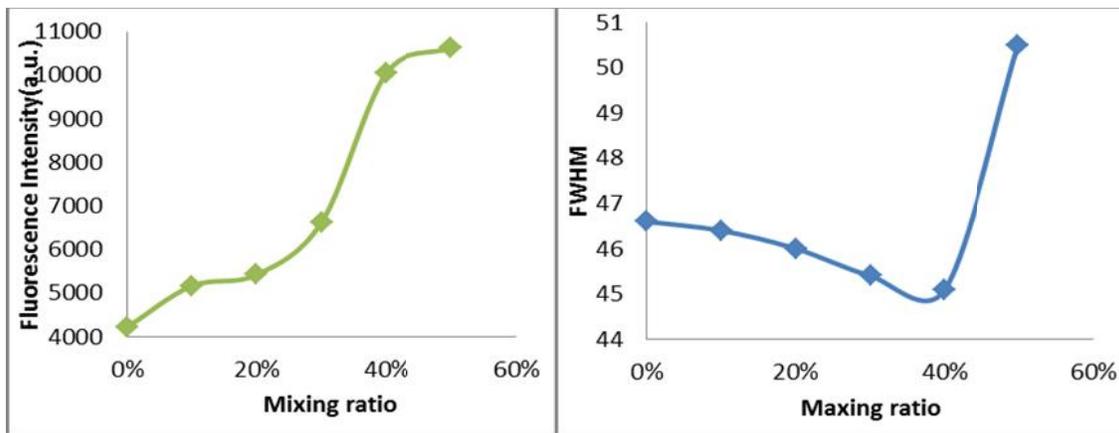


FIGURE 6: total peak fluorescence intensity of AgNP (5min) & R610 dye mixture in sol-gel rod

FIGURE 7: total FWHM of fluorescence intensity of AgNP (5min) & R610 dye mixture in sol-gel rod

TABLE 1: show the values of peak position, peak Fluorescence intensity and enhancement factor of AgNP (5 min) & R610 dye mixture at different mixing ratio in sol-gel rod.

Mixing ratio AgNP (5min) & R610	Peak Position(nm)	Fluorescence Intensity (a.u.)	FWHM	Enhancement Factor
R610 dye only	608	4221	46.6	-
10%	603	5169	46.4	1.22
20%	603	5426	46	1.28
30%	601	6638	45.4	1.57
40%	600	10056	45.1	2.38
50%	598	10622	50.5	2.51

By the same way the fluorescence spectra of R610 dye which is mixed with AgNP colloidal (10 min) as a reduction periods and incorporating it into sol-gel mixture as it illustrated in figure 8 below.

From figure 8 and table 2, it can be observed shifting in the peak position of fluorescence spectra toward short wavelengths (blue shift) until it reach to 601nm compared with dye only, and this shifting is less if it compared with the case of (5min) AgNP. From figure 9 one can notice that the increasing in fluorescence intensity is not fixed, maximum fluorescence intensity happened at 50%AgNP-

50% R610 mixing ratio with enhancement factor **1.56**, the second enhancement factor was occurred at 10% AgNP as a mixing ratio. Figure 10 shows the clear decreasing in value of FWHM with increasing the fluorescence. The effect of AgNP (10min) on R610 dye is less than it in the case of AgNP (5 min) whereas in the case of (5min) AgNP the maximum enhancement factor reached at **2.51**. The enhancement that is happened in the fluorescence intensity after adding the AgNP to the dyes may be attributed to the work of the added nanoparticles as a multiple scattering centers inside the host.

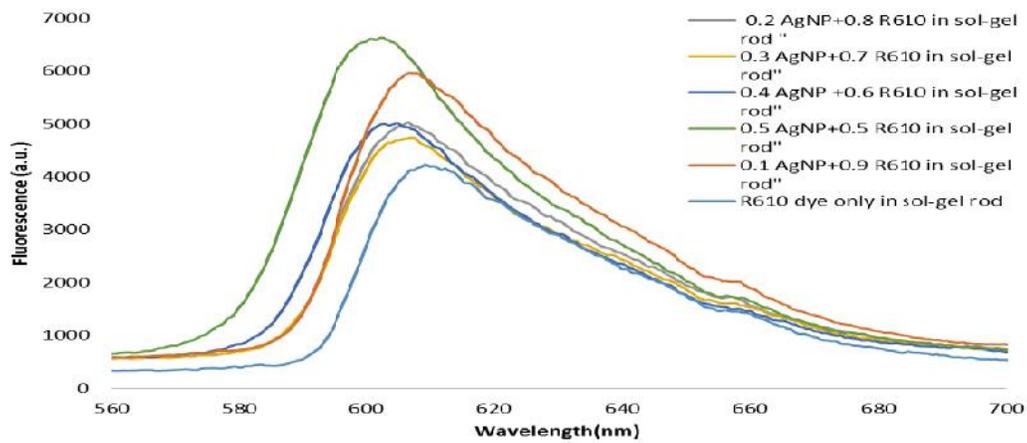


FIGURE 8: total fluorescence of AgNP (10 min) and R610 mixture in sol-gel rod at different mixing ratio

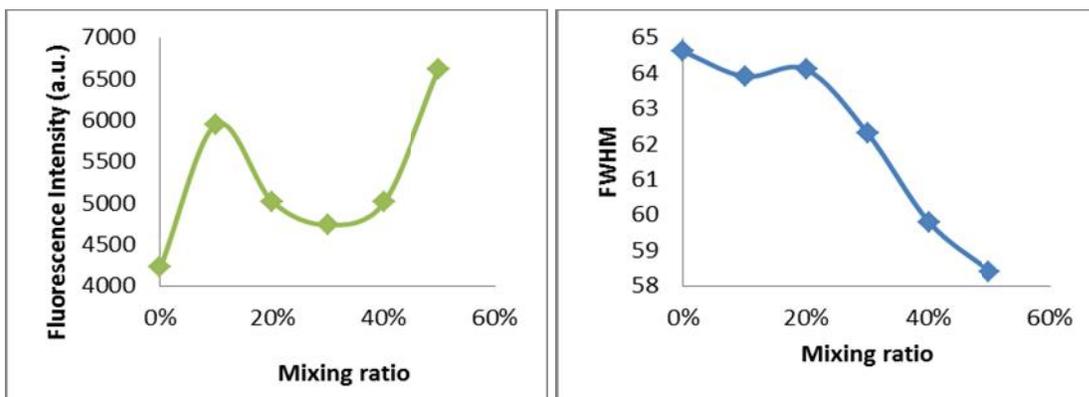


FIGURE 9: total peak fluorescence intensity of AgNP (10 min) & R610 dye mixture in sol-gel rod

FIGURE 10: total FWHM of fluorescence intensity of AgNP (10 min) & R610 dye mixture in sol-gel rod

TABLE 2: show the values of peak position, peak Fluorescence intensity and enhancement factor of AgNP (10minutes) & R610dye mixture at a different mixing ratio in the sol-gel rod

Mixing ratio	Peak Position (nm)	Fluorescence Intensity (a.u.)	FWHM	Enhancement Factor
R610 only	608	4221	64.6	-
10%	606	5950	63.9	1.40
20%	606	5018	64.1	1.18
30%	606	4734	62.3	1.12
40%	604	5008	59.8	1.18
50%	601	6620	58.4	1.56

CONCLUSION

Silver nanoparticles (5 and 10) min as a reduction periods effected on fluorescence intensity of R610 dye which incorporated into sol-gel matrixe and cause to enhance this fluorescence. The enhancement of R610 dye mixed with (5 min) as a reduction period of AgNPs colloid was higher than enhancement when the dye mixed with 10 min reduction period of AgNP. This maximum enhancement factor has been observed when 50% as a mixing ratio of (5 min) AgNPs colloid was added to R610. Where is equaled to 2.51. While maximum enhancement factor was 1.56 when 50% as a mixing ratio of (10 min) AgNPs colloid was added to R610

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