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Effect of Silver Nanoparticles on Fluorescence Spectra of C480 dye

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Abstract

This work aim to study the effect of silver nanoparticles on fluorescence intensity of Coumarin 480 dye by using the sandwiches technique where AgNP layer had been separated from C480 layer by different type of materials such as silica, PMMA polymer and PVA polymer layer. Silver nanoparticles had been prepared by the chemical reduction method so the AgNP layer coating had been done by hot rotation liquid method. The optical properties of prepared samples had been tested by using UV-VIS absorption spectrophotometer and Fluorescence spectrophotometer. Morphology, average size and the structure of nanoparticles were estimated using AFM, SEM testes

Keywords: Chemical reduction method, silver nanoparticle, metal enhance fluorescence.

تأثير جسيمات الفضة النانوية على شدة الفلورة لصبغة كومارين 480

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الخلاصة

يهدف هذا العمل الى دراسة تأثيرجسيمات الفضة النانوية على شدة الفلورة لصبغة كومارين 480 بأستخدام تقنية الساندويج وفيها طبقة الفضة النانوية مفصولة عن صبغة الكومارين 480 باستخدام مواد مختلفة مثل سيليكا, PMMA,PVA .جسيمات الفضة النانوية حضرت بطريقة الاختزال الكيميائي لذا فأن طبقات الفضة النانوية رسبت بطريقة السائل الدوار الحار. تم فحص الخصائص البصرية للعينات المحضرة باستعمال مطياف الامتصاصية ومطياف الانبعاثية. وتم فحص الشكل ومعدل الحجم والتركيب لجسيمات النانوية بواسطة مجهر القوة الذرية (AFM)و المجهر الالكتروني الماسح (SEM).

Introduction

Nobel Metals Nanoparticles such as Ag and Au NPs have been a source of great interest due to theirs applications in all branches of life, and due to their novel electrical, optical, physical, chemical and magnetic properties [1].metal nanoparticles have been prepared using many methods such as laser ablation technique [2], chemical reduction method [3], photo-reduction [4], arc-Discharge method [5] and Electrochemical Method [6]. Silver nanoparticles exhibit new optical properties, which are observed neither in molecules nor in bulk metals. Silver nanoparticles have an absorption band in visible light region. This band appears due to the surface plasmon- oscillation modes of conduction electrons [7]. The optical properties of nanomaterials depend on different parameters such as feature size, shape, surface characteristics, and other variables, including doping and interaction with the surrounding environment or other nanostructures [8].

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

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of silver salts by sodium citrate [9]. Recently fluorescence has many applications in the life sciences because of its sensitivity, and versatility variety of methods have been developed for enhanced fluorescence to increase the sensitivity of fluorescence. Surface Enhanced Fluorescence (SEF) has been the most widely investigated and explored. SEF 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. The changes in the fluorescent properties of fluorophores due to the presence of metal nanoparticles in the vicinity of these fluorophores [10]. Silver NPs are one of the most frequently used metals for fluorescence enhancement [11]. (SEF) enhancement is a maximum at a specific distance from the surface. After the metallic nanostructure supporting Local Surface Plasmon Resonance LSPR has been fabricated, an appropriate spacer layer should be found that maximizes the SEF enhancement of the target molecule [12].

Dyes are organic molecules. Coumarin dyes are well-known laser dyes for the blue-green region. The Coumarin dyes usually show very strong solvent polarity dependent Stokes' shifts substantial changes in the dipole moments while undergoing electronic transitions, and very high fluorescence quantum yields [13]

This paper focuses on enhancement of fluorescence intensity of a dye, the dependence of the fluorescence on NP diameter. Our model system consists of spherical silver NPs, surrounded by a silica or PMMA or PVA as a spacer layer, to which is attached the fluorescent dye.

Experimental Work

1. Materials

Silver nitrate and sodium citrate were received from Sigma Aldrich, Coumarin 480 dye from lambda physics, Poly Vinyle Alcohol (PVA), Poly Methyle Metha Acrylate (PMMA), distilled water, TEOS from Sigma Aldrich , these materials had been used without further purification.

2. Preparation of Silver Nanoparticles Films 0.0425 gm of $AgNO_3$ in 50mL deionized H_2O to prepared 50 ml as a starting solution of ~ 5.0 $\times 10^{-3}$ M of $AgNO_3$ in water, in order to reach 10^{-3} M concentration,25ml of $AgNO_3$ solution was added to 100ml of H_2O (now ~1.0 x 10^{-3}M). In another hand a solution of 1% sodium citrate (0.5 gm in 50ml of H_2O) has been made, then heated the 125ml solution of $AgNO_3$ until it begins to boil at 97 $^{\circ}$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 yellow and finally becomes dark brown that's an indication to silver nanoparticles creation with different particle size.

Silver nanoparticles had been coated onto glass microscope slide by using hot rotation liquid method [14].dipping the microscope slide perpendiculy in the hot rotation silver NP liquid for a different period's time from 5 to10 minutes as shown in Figure-1.

Figure 1-AgNP deposited on glass microscope slides by putting the slide in the hot rotation Ag NP solution at different reduction period

3. Preparation of Spacer Layer

3.1 preparations of silica layer

Using the sol-gel method, 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 mold, a catalyst solution containing deionized water , mixed with pure ethanol at volume ratio2:1 denoted as sol (B).then The sol (B) were slowly added to sol (A) with shake to ensure homogeneity, then 1ml of N-N dimethylformamide was added**.** Using the spin coating method to deposition this Silica as a second layer above silver nanoparticles coated slide, than prepared film in oven 70°C for one day.

3.2 preparation of PMMA polymer

The polymer Poly Methyle Metha Acrylate (PMMA) is a transparent plastic material with high elasticity, its resistance to climate changes is better than other polymers, and its optical properties are very good. It can be used as layer separated between the dye and silver nanoparticle, so 0.3 g from PMMA polymer was measured**,** dissolved in 30 ml of chloroform**,** and still stirrer until complete dissolving then the PMMA had been coated onto silver slide by using spin coating method at 3000 r.p.m.

3.3 preparation of PVA polymer

30 ml of distilled water was heated to 70^{o}C, at this degree 0.3gm of PVA polymer has been added to it, it rotates by a stirrer for one hour in order to obtain a completely dissolved solution, and then the PVA had been coated onto silver slide by using spin coating technique at 3000 r.p.m**.** too.

4. Structure and Optical measurements

The optical features were investigated by UV-Vis spectroscopy for AgNP film and Fluorescence spectroscopy for Ag-spacer-C480 sandwich . The surface roughness and topography of deposited thin films were studied by AFM, additionally SEM was employed to confirm the NPs shape, size and particle size distribution.

5. Results and Discussion

5.1 The Atomic Force Microscope (AFM) analysis of silver nanoparticles

The AFM is an instrument capable of measuring the topography of a given sample, Figure-2 show the atomic force microscope results for AgNP which had been prepared at different reduction periods, one can observe that the particle size was varied from 68 to 128 nm, it is so difficult to controlling the grain size so it is a global problem but the particle size still in the nanoparticle range**.**

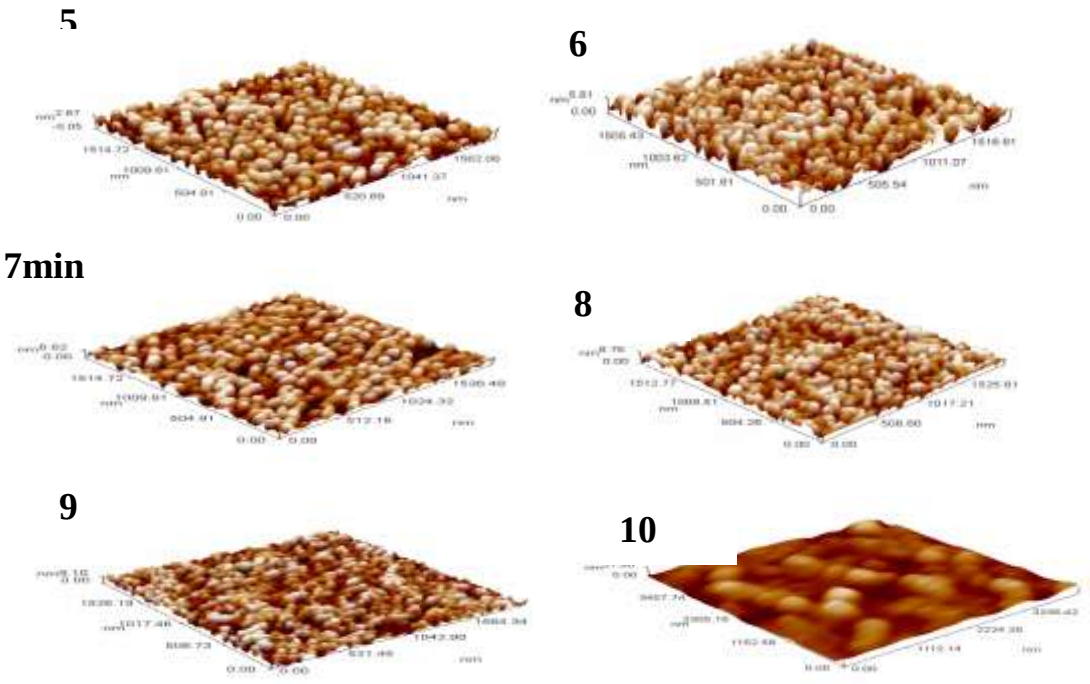

Figure 2- shows 3D images the AFM result for AgNP which is prepared by using different reduction period

5.2 SEM analysis of Silver Nanoparticles

SEM is a type of electron microscope, its powerful technique for analyzing the structure of the prepared metal nanoparticles, which produces images of a sample by scanning it with a focused beam of electrons. The information about the sample's surface topography, morphology, and composition of the obtained metal nanoparticles was examined by using scanning electron Microscope.

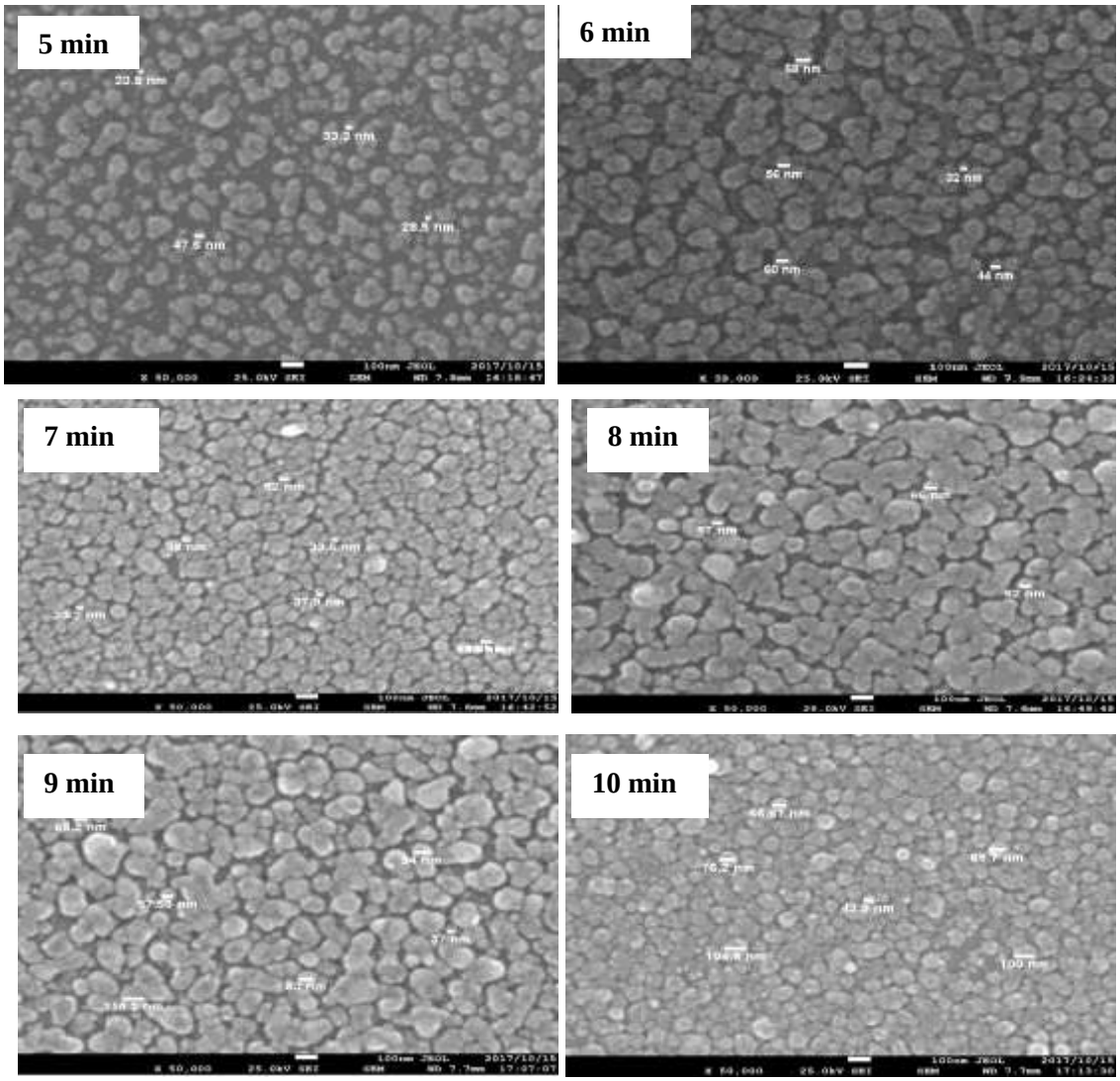

Figure 3-Shows the SEM image with magnification force = 50 kx of AgNP which had been prepared from 5 to 10 minutes as a reduction period.

By analysis the results of Figure-3 one can notice that at the case of 5 minutes a particle size at the range from 22.8 to 47.6 nm At the case of 6 minutes the particle size was distributed from 32 to 68 nm, in the case of 7 minutes the particle size was ranged between 33.2 to 56.8 nm, in the case 8 minutes the particle size was ranged from 57 to 66 nm at the case of 9 minutes the particle size was varied from particle size 37 to 115.2 nm and finally at the case 10 minutes the particle size was ranged from 42.9 to 104.8nm.These increasing in particles size may be due to the collapse of crystalline edges in conjunction with increasing the temperature of reduction

6. UV-Visible Spectrophotometer of Silver Nanoparticles

The absorption spectra of AgNPs films had been tested by using UV-Visible Spectrophotometer. All results were presented in Figure-4, its clearly to notice that the absorption was increased, with the increasing in reduction periods means that the AgNPs concentration was increased, as a consequence to that the absorbance increased.

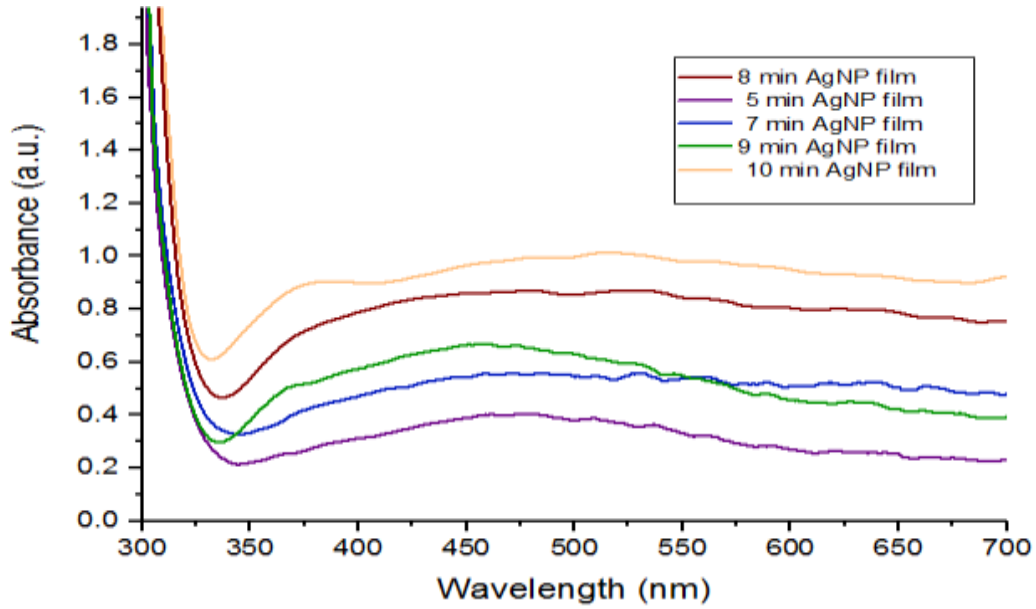

Figure 4-The absorbance spectra for silver nanoparticle film which is prepared by hot chemical reduction method as a function to reduction period.

7. Fluorescence Spectra Measurements

7.1Fluorescence spectra of Ag-silica- C480 sandwich

Our model system consists of spherical silver NPs separated from C480 dye film by silica layer as a spacer distance. From first sight to Figure-5 one can notice altering at the emission intensity of the dye.

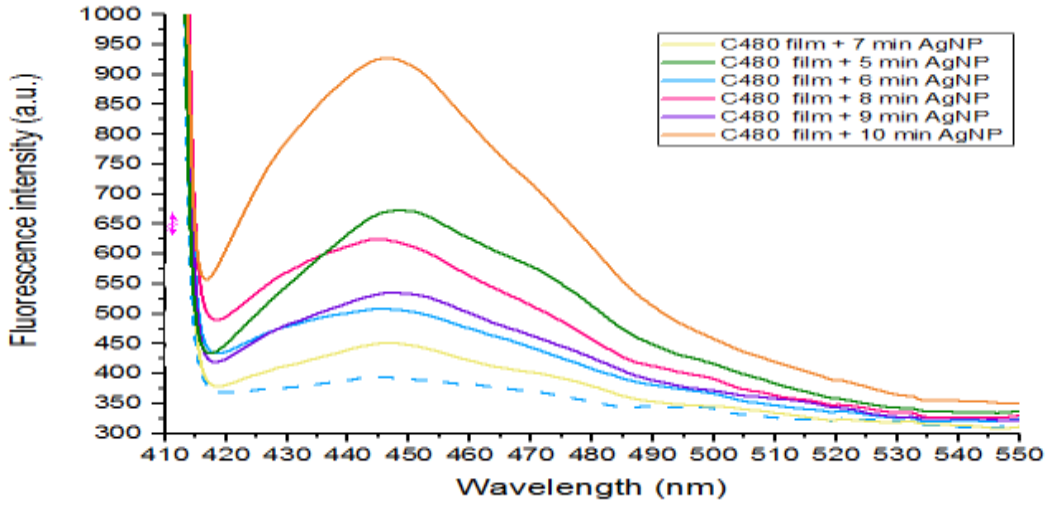

Figure 5-metal enhance fluorescence of AgNP-silica -C480 sandwich (different reduction period).

Which show the fluorescence emission spectra of Ag-silica-C480dye sandwich substrate, the particle size of AgNP was increased as shown in SEM examination Figure-3 with increasing reduction period from 5 to10 minutes. The peaks position of fluorescence spectra for different reduction periods ranging between 444.5 to 446.3 that mean the peak position located at a fixed point. The silica coating was thin enough to provide the optimal distance for enhancement. In other words, metal nanoparticles were far from C480 molecules for energy transfer, but C80 molecules are near from the electromagnetic field of surface plasmons.

Table-1 shows the enhancement in the fluorescence intensity versus Ag particle size, which reached maximum at 10min AgNP with Enhancement factor 2.34. This behavior may be due to the remarkable optical properties displayed by metal nanostructures, in particular the coupling between

the free electrons responsible for surface plasmon resonance and nearby fluorophores can enhance the emission rates and decrease the lifetimes of excited states. This phenomenon termed metal-enhanced fluorescence (MEF) as agreement with [15].

Table 1- shows the values of peak position, Fluorescence intensity and enhancement factor of AgNP-silica-C480 sandwich using metal enhance fluorescence

AgNP and C480	Peak Position (nm)	Fluorescence Intensity (a.u.)	Enhancement Factor
C480 dye only	444.5	394.8	
5	448.5	673.3	1.70
6	445.8	509.1	1.28
7	446.3	451.8	1.14
8	444.5	624.8	1.58
9	446.7	535	1.35
10	446.3	927.7	2.34

7.2Fluorescence spectra of Ag-PMMA- C480 sandwich

All procedure was same in the first case except that the silica had been replaced by PMMA layer. By using PMMA as a spacer, it was observed from Figure-6 that the maximum enhancement was about 1.47 in contrast to the silica in which enhancement was reached to 2.34. Table-2 shows the enhancement in the fluorescence intensity versus Ag particle size which reached maximum at 8min AgNP with

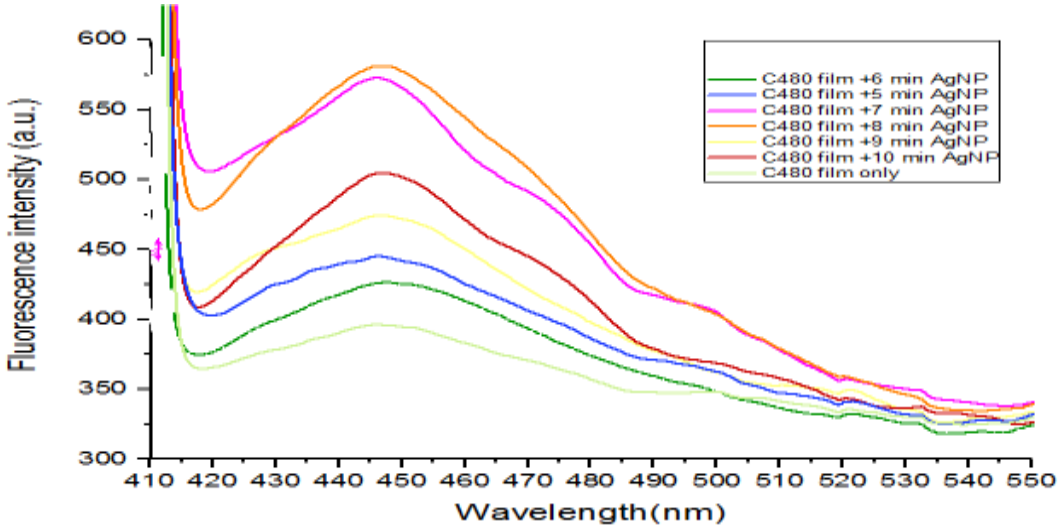

Figure 6-metal enhance fluorescence of AgNP-PMMA -C480 sandwich (different reduction period) Enhancement factor 1.47.

Table 2-show the values of peak position, Fluorescence intensity and enhancement factor of AgNP-PMMA-C480 sandwich using metal enhance fluorescence

AgNP and C480	**Peak Position**	**Fluorescence intensity (a.u.)**	**Enhancement Factor**
Dye only	**444.5**	**394.8**	**-**
5	**446.3**	**445.3**	**1.12**
6	**445.4**	**396.2**	**1**
7	**445.8**	**572.9**	**1.45**
8	**447.6**	**581.2**	**1.47**
9	**446.3**	**474.4**	**1.20**
10	**446.3**	**504.6**	**1.27**

7.3Fluorescence spectra of Ag-PVA- C480 sandwich

Here PVA was used as a spacer layer. as observed in the Figure-7 it has been obtained a variable behavior between enhance at the case of using 5, 6, 7, 10 minutes as a reduction period and quenching at the case of 8, 9 minutes as a reduction period.

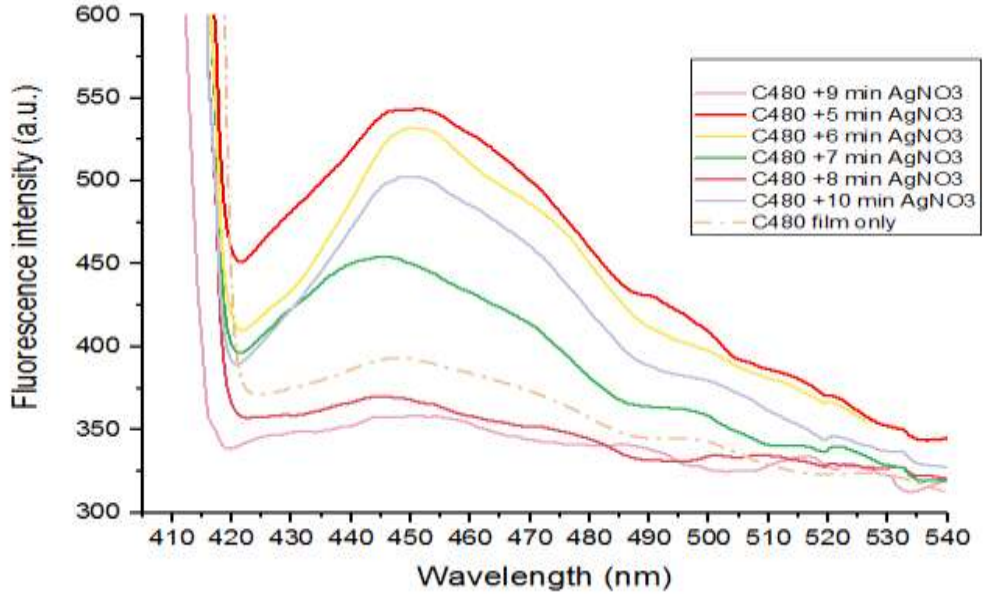

Figure 7-metal enhance fluorescence of AgNP-PVA -C480 sandwich (different reduction period).

Table 3-show the values of peak position, Fluorescence intensity and enhancement factor of AgNP-PVA-C480 sandwich using metal enhance fluorescence

AgNP and C480	Peak Position	Fluorescence intensity (a.u.)	Enhancement Factor
Dye only	**444.5**	**394.8**	
5	**451.1**	**543.4**	**1.37**
6	**450.2**	**531.9**	**1.34**
7	**445.4**	**454.3**	**1.15**
8	**445.8**	**370.1**	**-**
9	**451.6**	**358.6**	**-**
10	**449.3**	**502.8**	**1.27**

Table-3 shows the maximum enhancement factor was 1.37 at 5 min AgNPs as a reduction period.

Conclusion

The best enhancement was observed when silica layer used as a spacer distance between AgNPs and the fluorophores of C480 dye. The maximum enhancement factor has been observed at the case of using 10 minutes as a reduction period of AgNPs. Where the enhancement factor equaled to 2.34. From the results of the calculation of enhancement factor for different spacer type such as silica, PMMA and PVA, one can conclude that the best spacer is silica if it compared with the enhancement factor of PMMA and PVA.

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