# Effect of Ag nanoparticles on R6G laser dye hosted by PMMA polymerized by plasma jet

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## Abstract

This work aim to prepare Ag/R6G/PMMA nanocomposite thin films by In-situ plasma polymerization and study the changes in the optical properties of fluorophore due to the presence of Ag nanoparticles structures in the vicinity of the R6G laser dye. The concentrations of R6G dye/MMA used are: $10^{-4}$M solutions were prepared by dissolving the required quantity of the R6G dye in MMAMonomer. Then Silver nanoparticles with 50 average particles size were mixed with MMAmonomer with concentration of 0.3, 0.5, 0.7wt% to get R6G silver/MMA in liquid phase. The films were deposited on glass substrates by dielectric barrier discharge plasma jet. The Ag/R6G/PMMA nanocomposite thin films were characterization by UV-Visible absorption spectra by using a double beam UV-Vis-NIR Spectrophotometer and fluorescence Spectrophotometer. The thin films surface morphological analysis is carried out by employing an AFM and SEM. the structure analysis are achieved by X-ray diffraction. The thickness of the films was measured by optical interferometric method. AFM analysis shows that the surface roughness of plasma polymerized pure PMMA thin films was 2.7 nm and for ($10^{-4}$ R6G + 0.7wt% Ag)Ag/R6G/PMMA thin films was 4.16 nm. The SEM images were indicates that Ag nanoparticles (NPs) disperse in the PMMA matrix with uniform distribution and formed mostly spherical NPs and slightly agglomerate. Also the silver nanoparticles with 0.7wt% concentration enhances the absorption process by 2.3 times and the fluorescence by 1.7 times. it can be conclude, that the addition of low concentrations of silver nanoparticles to the PMMA/ R6G matrix was changing the optical properties of the prepared nanocomposite thin films.

**Key words**

*Plasma jet, Ag/R6G/PMMA nanocomposite, R6G laser dye.*

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# تاثير جسيمات الفضة النانوية على الصبغة الليزرية R6G المحتوات في بوليمر PMMA المبلمر ببلازما النفث

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## الخلاصة

يهدف هذا العمل الى تحضير اغشية رقيقة لمتراكبات نانوية (Ag/R6G/PMMA) بواسطة البلمرة بالبلازما ودراسة التغييرات في الخواص البصرية للصبغة بسبب وجود جسيمات الفضة النانوية بالجوار من الصبغة الليزرية (R6G) والتحكم بالخصائص البصرية (معامل الانكسار، الامتصاصية، طيف الفلورة وغيرها) لاغشية (Ag/R6G/PMMA). تمت بلمرت مونيمر (MMA) السائل بواسطة بلازما.التركيز الذي استعمل

في تحضير اغشية (R6G/PMMA) المبلمرة بالبلازما نفث هي $10^{-4}$(mole/liter) المحلول السائل حضر باذابة الكمية المطلوبة من الصبغة الليزرية (R6G) في المونمر السوائل (MMA) بعدها تم خلط جسيمات الفضة النانوية معدل حجم جسيماتها 50 nm بتراكيز (0.3, 0.5 and 0.7 wt %) مع المحلول السائل للحصول على خليط (فضة صبغة مونمر) في الطور السائل. الاغشية تم ترسيبها على شرائح زجاجية بواسطة البلازما نفث. استعملت تقنيات تحليلية مختلفة لدراسة تركيب وبنية الاغشية وخصائصها البصرية اذ قيست الخصائص البصرية للاغشية الرقيقة بواسطة UV-Visible و Fluorescence Spectrophotometer واستعملت AFM و SEM لدراسة التركيب السطحي وحيود الاشعة السينية لتحليل البنية التركيبية الهندسية للاغشة وقيس السمك للاغشية بطريقة التداخل البصري.اظهر تحليل ال AFM نعومة سطح الغشاء المتبلمر بالبلازما للبوليمر النقي (PMMA) بحدود 2.7 nm ولغشاء ($10^{-4}$ R6G + 0.7wt% Ag PMMA) كان بحدود 4.16 nm. واظهرت صور الماسح الالكتروني المجهري (SEM) جسيمات الفضة النانوية متوزعة بصورة متجانسة في حجم الغشاء وذات اشكال كروي لاغلب الجسيمات وذات تكتل قليل. و اظهرت الاغشية التي فيها الفضة بتركيز 0.7wt% وتركيز الصبغة $10^{-4}$(mole/liter) تعزيز في المتصاص بلغت قيمتة 2.3 مرة و تعزيز للفلورة بمقدار 1.7 مرة. واظهر نمط حيود الاشعة السينية لغشاء البوليمر النقي بانه ذو بنية تركيبية عشوائية والاغشية التي فيها جسيمات فضة ظهر في طيف حيودها قمم حيود حادة تتوافق مع الطور الرئيسي لجسيمة الفضة النانوية ذات التركيب البنائي المكعب. يمكننا ان نستنتج ان اضافة تراكيز قليلة من جسيمات الفضة النانوية لمصفوفة R6G/PMMA قد غير الخصائص البصرية للاغشية الرقيقة المحضرة.

## Introduction

In recent years, a noble metal nanoparticle such as silver is of great significant due to size dependent optical properties [1]. These unique properties could be attributed to their large specific surface area. The metallic nanoparticles have been used in many applications in photonics. PMMA and others Polymers are considered to be an excellent host material for nanoparticles of Ag metals [2]. The obtained nanocomposites might exhibit enhanced optical properties [3]. However, the properties of polymer composites depend on concentration, type of funded nanoparticles, as well as their size and shape, and how it interaction with the polymer matrix. Among polymer materials, PMMA is well known as a polymeric with a wide range of applications. Use of PMMA offers many advantages such as availability to carboxylate functional group for a chemical bonding with the metal ions, high solubility of PMMA in solvent and high transparent in the UV-Visible. Dyes are organic molecules. Fluorescent dyes have conjugated double bonds (saturated hydrocarbons) and attached to the molecules are mesmeric functional groups, fluorophores, which are responsible for photon absorption and emission. The molecules reemit photons of lower energy after absorbing photons of higher energy due to radiative transition. As the structure of the molecular energy level does not change during the absorption the emission spectrum is mirror image of the absorption spectrum and red shifted. The fluorescent dye, R6G, used in the present work is from the class of xanthene dyes. R6G has fluorescent bands in the visible region of the spectrum. The photophysical properties of laser dyes in various solid matrices have been attracting a significant concern in view of their wide range of applications such as tunable solid-state dye lasers, energy transfer experiments, and development of random laser [4].

Recently fluorescence has many application in life sciences because of its sensitivity, and versatility variety of methods have been developed for enhanced fluorescence to increase the sensitivity of fluorescence, noble metal enhanced fluorescence (MEF) has been the most widely investigated and explored. The changes in fluorescent properties of fluorophores due to this MEF include increased rates of excitation, and decreased fluorescence lifetimes. The presence of meatal nanoparticles structures in the vicinity of the fluorophore can alter the optical properties of the fluorophore by increasing the excitation field depending on the distance between the metal nanoparticle and fluorophore [5, 6]. The noble metals in the form of nanoparticles could significantly enhance fluorescence [7, 8].

Thin film can be prepared by so many approaches like spin coating, chemical bath deposition thermal evaporation etc., but plasma polymerization technique of preparation of thin film is another approach, in which monomer can be converted to polymer in presence of glow discharge [7]. This work aims to prepare Ag/R6G/PMMA nanocomposite thin films by In-situ plasma polymerization and study the changes in the optical properties of fluorophore due to the presence of Ag nanoparticles structures in the vicinity of the R6G laser dye.

## Experimental work

### 1. Plasma deposition of R6G/ silver/ PMMA Nanocomposite thin films

R6G/ silver/ PMMA nanocomposite thin films were prepared by dielectric barrier discharge plasma jet. The concentrations of R6G dye/MMA used is: $10^{-4}$M solutions were prepared by dissolving the required amount of the R6G dye in Monomer (MMA) for (7-10) days to complete melting. Then Silver nanoparticles from Nanjing nano Technology co, ltd, China its particle size was 50nm and purity of 99.9%, were mixed with (MMA) monomer with concentration of 0.3, 0.5 and 0.7wt% to get R6G silver/MMA in liquid phase. The mixture dispersed for one hour by ultrasonic to ensure a homogeneous distribution of nanoparticles. The films were deposited on glass substrates by dielectric barrier discharge plasma jet. The schematic diagram for the non-equilibrium atmospheric pressure plasma nanocomposite thin films preparations shows in Fig.1. Argon gas passes through the nebulizer which contains MMA Monomer the monomer convert to aerosol, this aerosol was guided by the Ar gas to the plasma jet, and the plasma was ignited by using an electric source at a fixed frequency of 35 kHz. The plasma was generated downstream to the substrate which was positioned along fixed distance from the plasma torch end which was 2 cm. The film deposition was carried out for 5min. The substrate moved on the x and y direction mechanically for the purpose of obtaining a homogeneous films thickness along the substrate area.

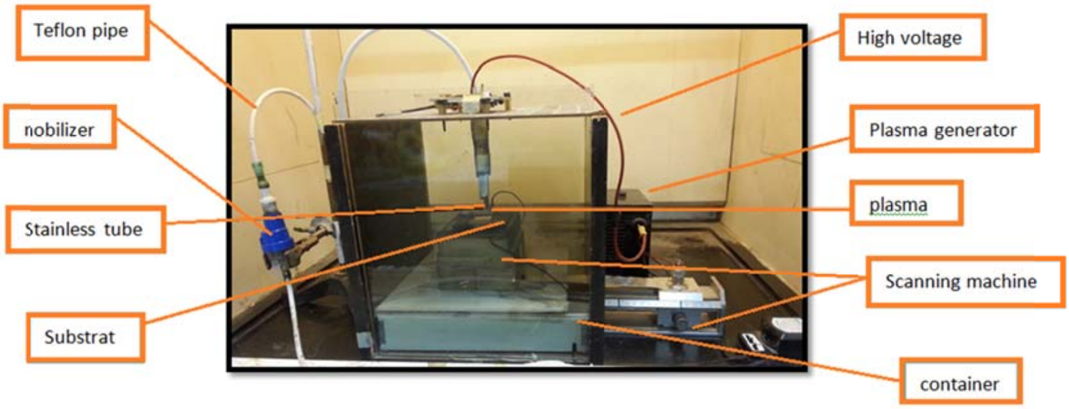


*Fig.1: Photographic image for non-equilibrium atmospheric pressure plasma jet polymerization experimental set-up used in the present work.*

## 2. Thin films characterization

UV-Visible absorption spectra of pure PMMA and R6G/ silver/ PMMA nanocomposite thin films were obtained by using a double beam UV-Vis-NIR 210A Spectrophotometer.and the fluorescence by fluorimeter and the exaction wavelength was 530 nm. The thin films surface morphological analysis is carried out by employing an Atomic Force Microscope(AFM) andSEM. the structure analysis are achived by X-ray diffractometer system. The thickness of the films was measured by optical interferometric method.

## Results and discussions

## 1. X-ray diffraction for pure PMMA and R6G/ Ag/ PMMA thin films

Fig. 2 shows the x-ray diffraction pattern of the prepared PMMA thin film and Fig. 3 for the R6G/ Ag/ PMMA with concentration ($10^{-4}$ R6G + 0.7wt% Ag) nanocomposite thin films. Table 1 shows the thin films preparation conditions. From the x-ray diffraction pattern it is clearly indicated that pure PMMA thin film has amorphous structure. Plasma polymers are usually amorphous in nature, where made of short chains of monomers characterized by a high degree of cross-linking and dangling bonds. For the R6G/ Ag/ PMMA thin film all Miller Indices (hkl) reveal the FCC structure of Ag nanoparticles where the diffraction peaks at crystalline plans (111), (200), (220), and (311). All these patterns were analyzed by the Riveted method, using the refinement system for every pattern. All the reflections corresponded to the pure silver metal with cubic symmetry. The reflections presented by four main peaks at 2θ= 38.14, 44.27, 64.44 and 77.41°which are assigned to the lattice planes (1 1 1), (2 0 0), (2 2 0) and (3 1 1). Comparing these patterns with that of pure silver, 2θ for the crystalline plans (111), (200), (220), and (311) are 38.122, 44.284, 64.433 and 77.480.it conclusion that our samples are effectively contains Ag.

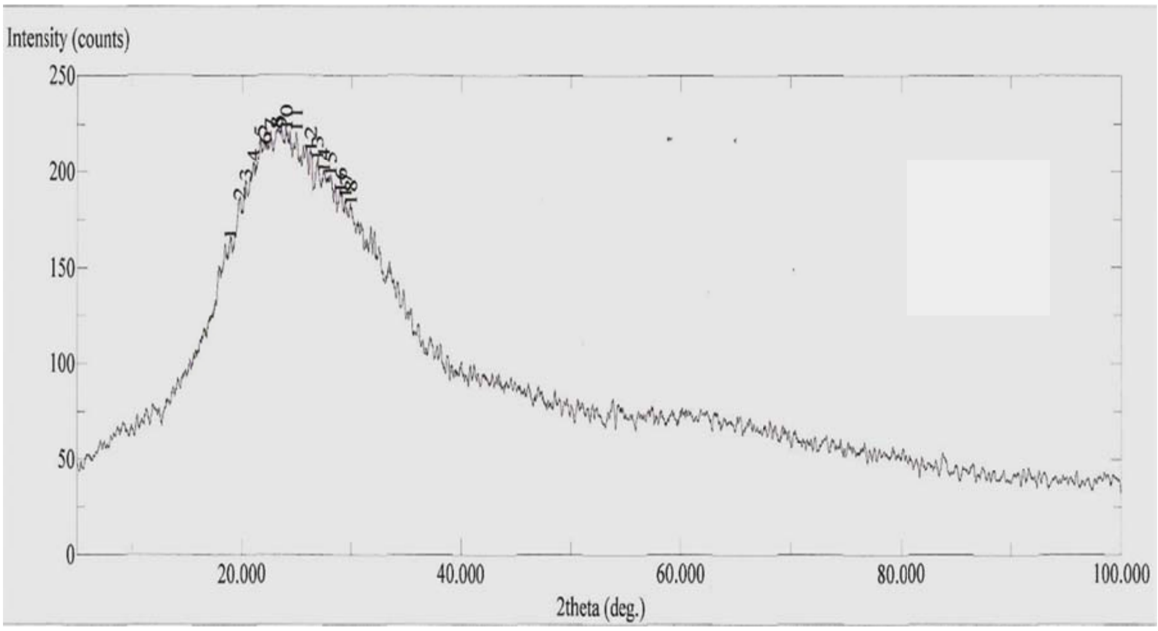


*Fig. 2: X-ray diffraction for pure PMMA thin film.*

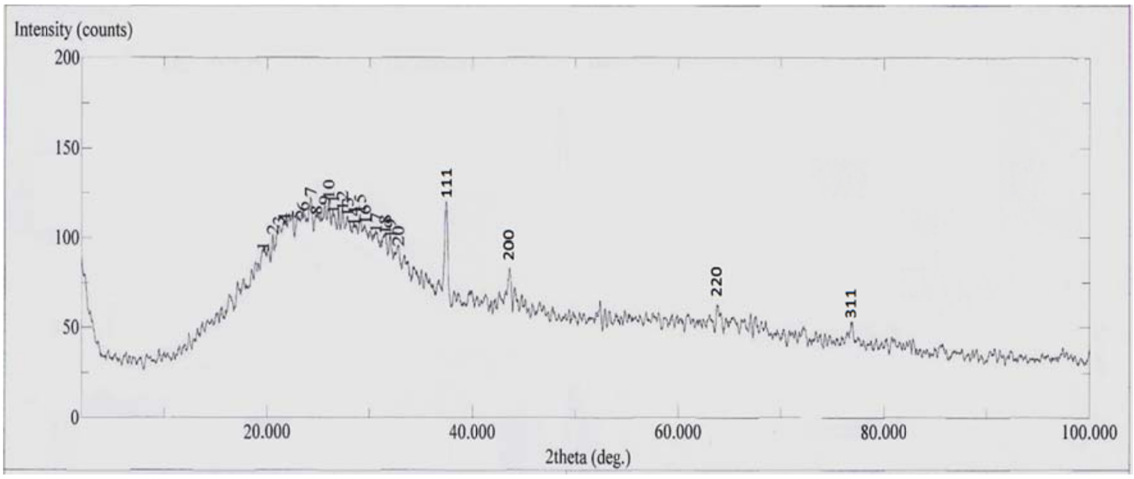


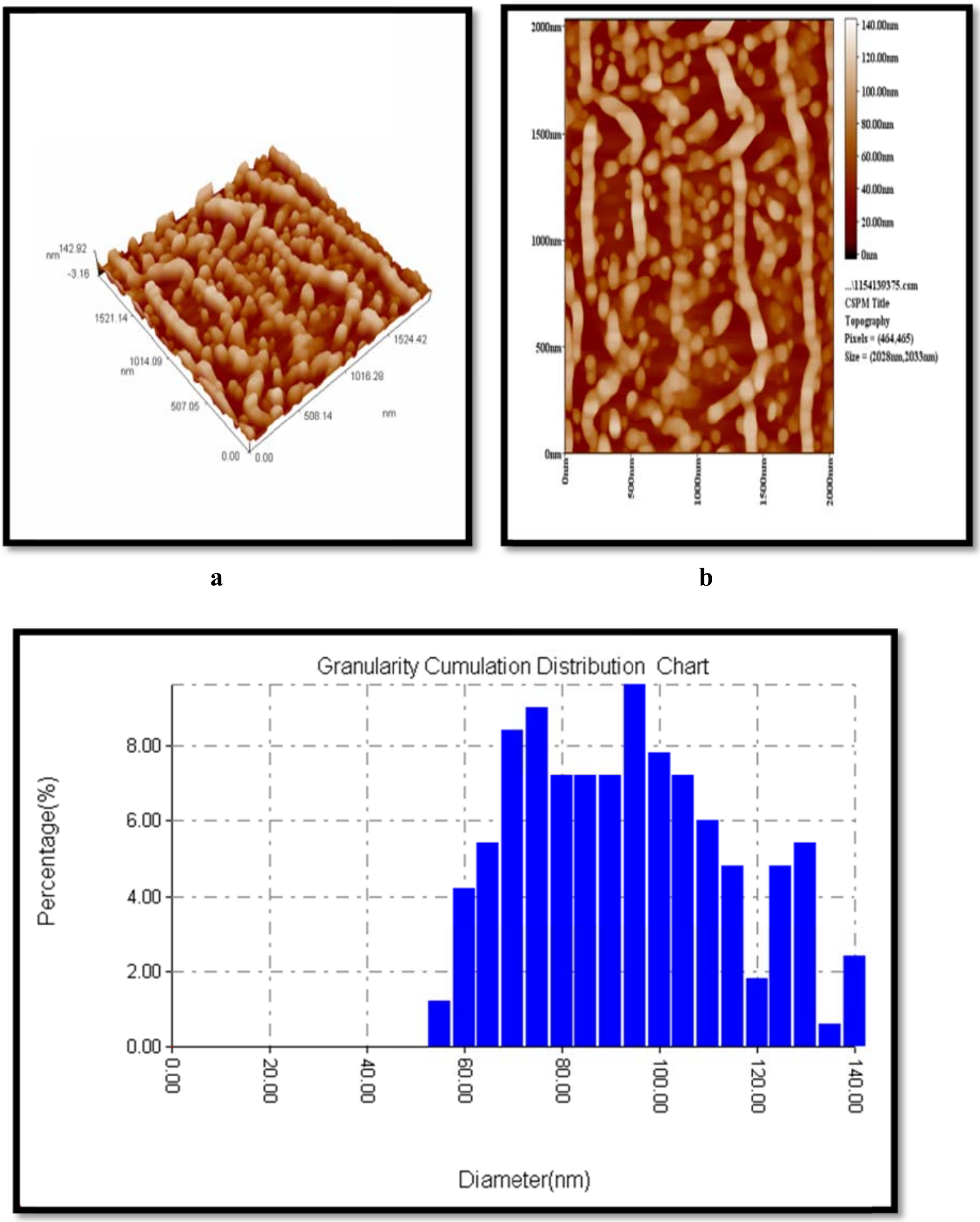
*Fig. 3: X-ray diffraction for 0.7wt% concentration R6G/Ag/ PMMA thin film.*

*Table 1: The experimental condition for the preparation of R6G/ silver/ PMMA nanocomposite thin films.*

| Dye concentration | Ag concentration | Thickness (nm) | Gas flow rate (L/min) | Distance (cm) |
|---|---|---|---|---|
| R6G $10^{-4}$M | without | 356 | 2 | 2 |
| | + 0.3 wt % Ag | 365 | | |
| | + 0.5 wt % Ag | 430 | | |
| | + 0.7 wt % Ag | 450 | | |

## 2. Surface morphology for pure PMMA and R6G/ Ag/ PMMA thin films

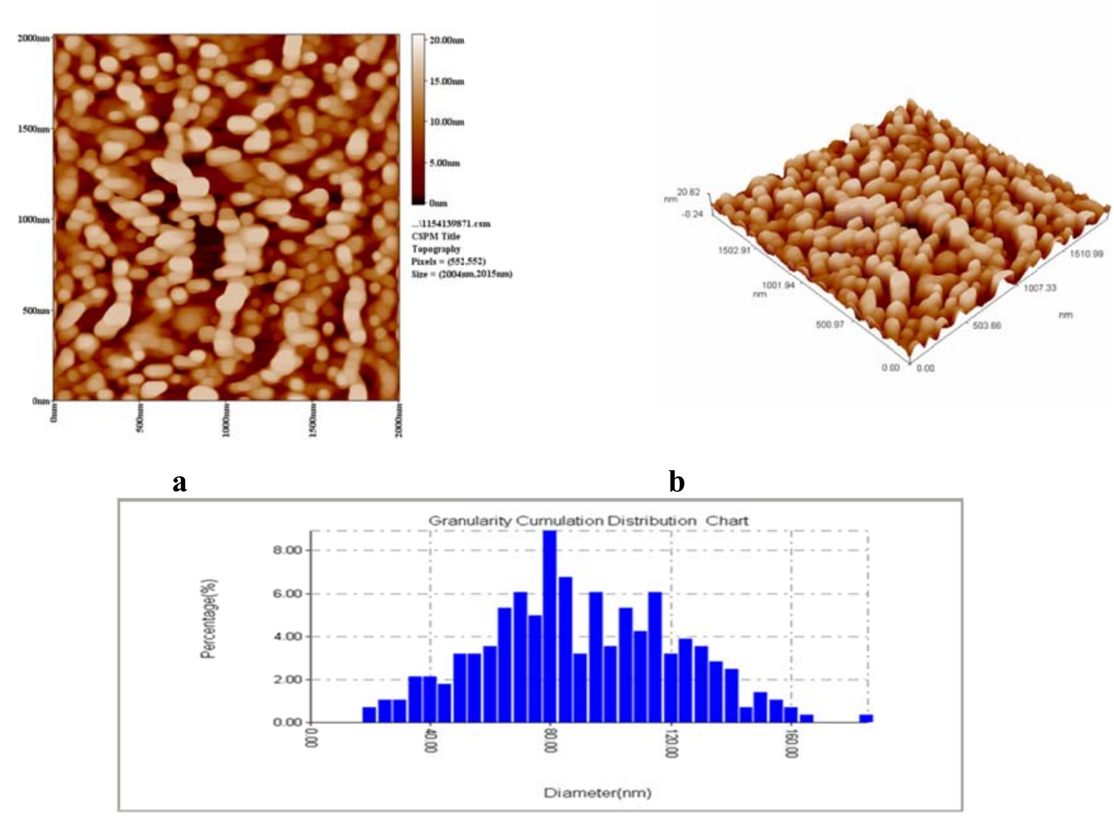
The surface morphology of the pure PMMA and R6G/ Ag/ PMMA with concentration ($10^{-4}$ R6G + 0.7wt% Ag) nanocomposite films were examined by AFM. The surface roughness of plasma polymerized pure PMMA thin films was 2.7 nm and for ($10^{-4}$ R6G + 0.7wt% Ag) thin films was 4.16 nm. The low surface roughness of plasma polymerized R6G/silver/ PMMA nanocomposite confirms that the technique of plasma polymerization can be employed to produce extremely smooth films with very small surface roughness when compared to films prepared by other techniques. It is clear that the silver nanoparticles are uniformly distributed within the scanning area. Figs.4 a and b represent the tilted and top view AFM photos of the pure PMMA thin film surface and **c** shows the granuality distribution chart. The average diameter of clusters is 91.23 nm. Figs.5 a and b represent the tilted and top view AFM photos of the ($10^{-4}$ R6G + 0.7wt % Ag) thin films surface and c shows the granuality distribution chart. The average diameter of clusters was 87.85 nm. The additions of silver nanoparticles were reducing the surface roughness of the nanocomposite thin films and this gives an indication that silver nanoparticles are uniformly distributed.



**a** **b**

**c**

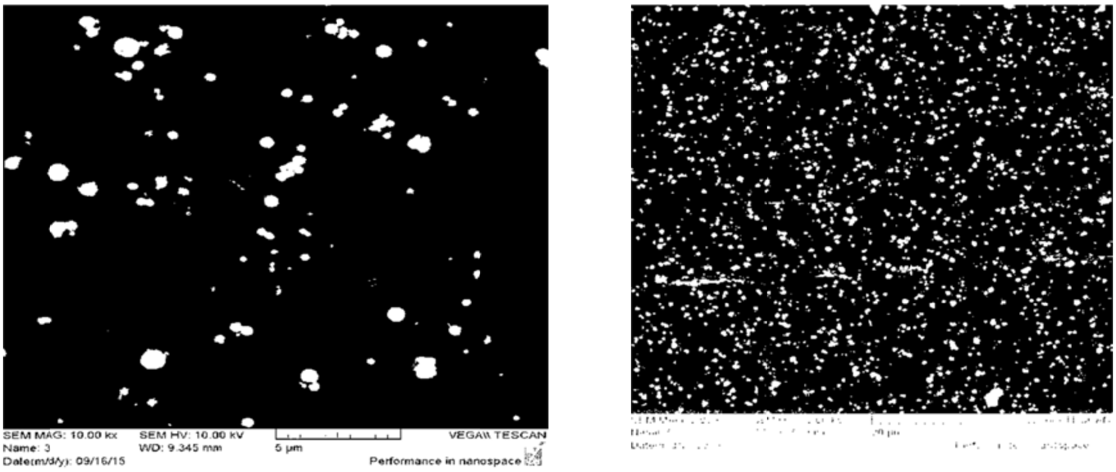
***Fig. 4: AFM photographs of PMMA film surface (a) top view, (b) tilted view, (c) the granularity distribution chart***



c

*Fig.5: AFM photographs ($10^{-4}$ R6G + 0.7wt % Ag) nanocomposite thin film surface (a) top view (b) tilted view, (c) the granularity distribution chart.*

The distribution and shape of Ag NPs were found by performing scanning electron microscopy(SEM). Figure (6a andb) shows the SEM images of R6G/ Ag/ PMMA nanocomposite thin film at ($10^{-4}$ R6G + 0.7wt % Ag) concentration. The SEM images were indicates that Ag NPs disperse in the PMMA matrix with a relatively uniform distribution and formed mostly spherical NPs and slightly agglomerate. The silver nanoparticles are homogeneously dispersed in the polymer R6G matrix.



a b

*Fig. 6: SEM image for R6G/ Ag/ PMMA nanocomposite thin film at ($10^{-4}$ R6G + 0.7wt %) Ag concentration in different magnification.*

## 3. UV-Visible study for R6G/ Ag/ PMMA thin films

The absorption spectra of R6G/ Ag/ PMMA nanocomposite thin films at $10^{-4}$ R6G concentration and different Ag nanoparticles 0.3, 0.5 and 0.7wt% concentration are shown in Fig. 7. The absorption spectra of nanocomposite thin films shows peak at 535 nm. It is observed that the absorption spectra show similar behavior for different Ag-concentrations. From the Figure it notes that the increase in silver concentration enhances the absorption process and Table 2 shows the enhancement in the absorption process versus the Ag concentration. This behave can be illustrated as follows. Plasmonic metal nanostructures have shown to be able to enhance optical processes. The enhancement effect of surface enhanced absorption is based on the excitation of localized surface plasmons giving enhanced electromagnetic fields. The molecules placed inside this enhanced field will be excited more often due to intensity enhancement of the incoming light without actually increasing the intensity of the light source.

*Table 2: The enhancement in the absorption process versus the Ag concentration.*

| Dye concentration | Ag concentration | Thickness (nm) | $\lambda_{Ab\ nm}$ | Absorbance value(arb.unt) | Absorbance enhancement |
|---|---|---|---|---|---|
| R6G $10^{-4}$(mole/liter) | without | 356 | 535 | 0.082192 | |
| | + 0.3 wt % Ag | 365 | 536 | 0.135845 | 1.7 |
| | + 0.5 wt % Ag | 430 | 538 | 0.155504 | 2 |
| | + 0.7 wt % Ag | 450 | 542 | 0.187999 | 2.3 |

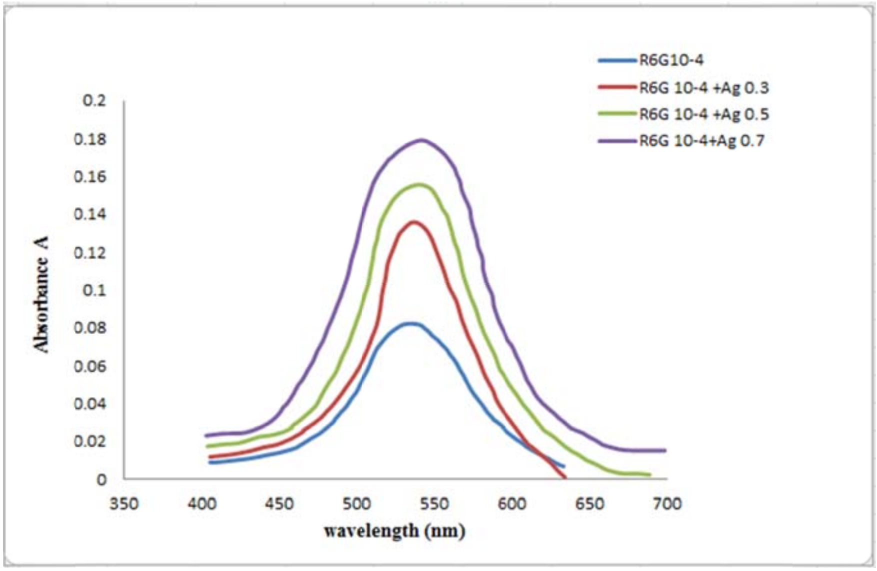


*Fig. 7: The absorption spectra of R6G/ Ag/ PMMA nanocomposite thin films at $10^{-4}$ R6G concentration and different Ag nanoparticles 0.3, 0.5 and 0.7wt% concentration.*

## 4. Photoluminescence study for R6G/ Ag/ PMMA thin films

Fig. 8 shows fluorescence emission spectra of R6G/ Ag/ PMMA nanocomposite thin films at $10^{-4}$ R6G concentration and different Ag nanoparticles 0.3, 0.5 and 0.7wt% concentration with exaction wavelength 530 nm. The emission peaks of fluorescence spectra have been observed at wavelengths (560, 568, 570 and 574) which lie in the visible region Table 3 shows the enhancement in the fluorescence emission spectra versus the Ag concentration. The intensity of peaks increases with increasing Ag nanoparticles concentration. This behavior may be due to the fact that enhanced fluorophore excitation can be gained by placing the fluorophore inside the enhanced electric fields around a plasmonic structure. Hereby the fluorophores suffer from a higher light intensity and more of them will be excited without increasing the intensity of the light source, As a result, more fluorophores in the excited state then automatically leads to a larger number of photons are emitted and a total enhancement of fluorescence compared to a system without the plasmonic structure.

*Table 3: The fluorescence emission enhancement versus the Ag concentration.*

| **Dye concentration** | **Ag concentration** | **Thickness (nm)** | $\lambda_{fluo}$ nm | **Fluorescence value (arb.unt)** | **Fluorescence enhancement** |
|---|---|---|---|---|---|
| R6G $10^{-4}$(mole/liter) | without | 356 | 560 | 2481.35 | |
| | + 0.3 wt % Ag | 365 | 568 | 3200.44 | 1.3 |
| | + 0.5 wt % Ag | 430 | 570 | 3826.18 | 1.6 |
| | + 0.7 wt % Ag | 450 | 574 | 4000.91 | 1.7 |

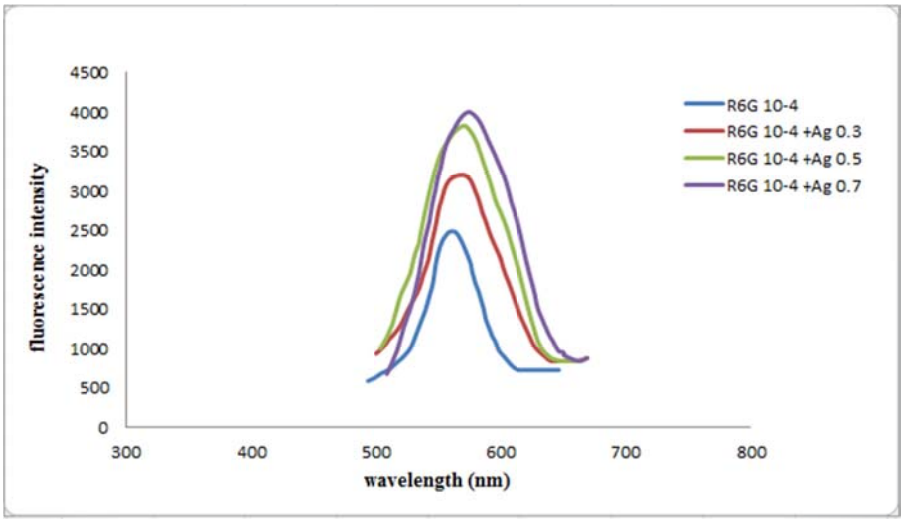


***Fig. 8: Fluorescence emission spectra of R6G/ Ag/ PMMA nanocomposite thin films at $10^{-4}$ R6G concentration and different Ag nanoparticles 0.3, 0.5 and 0.7wt% concentration.***

## Conclusions

The possibility of preparation R6G/ Ag/ PMMA nanocomposite thin films by In-situ plasma polymerization these thin films have very small surface roughness. The silver nanoparticles are homogeneously dispersed in the polymer R6G matrix. The addition of low concentrations of silver nanoparticles to the polymer R6G matrix was changing the optical properties of the prepared nanocomposite thin films. Where the additions of the silver nanoparticles to the nanocomposite were enhances the absorption process by 2.3times, and the fluorescence by 1.7 times. The preparation of R6G/ Ag/ PMMA nanocomposite thin films by In-situ plasma polymerization did not affect the optical properties (absorption and fluorescence) of the R6G dye which retained by its absorption and fluorescence peaks in the same position for the pure R6G dye.

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