Studying the Surface Morphology and Optical Properties of 4-Methylbenzenthiol Capped Gold Nanoparticles Films with Annealing

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Abstract:

Surface morphology and optical properties in term of Surface Plasmon Resonance (SPR) of 4-methylbenzenthiol capped gold nanoparticles using Langmuir-Schaefer (LS) technique were studied. 1 and 3-layers nanoparticle films with 1mg/ml in concentration have been prepared. Gold nanoparticles films were annealed at 200^{o}C for 1h. Film's morphology and SPR before and after annealing were investigated by Atomic Force Microscopy (AFM) and UV-Vis spectrophotometer respectively. After annealing, a drastic change in the shape and size of the nanoparticles was revealed; however, no significant effect of film thickness on the gold nanoparticle size was observed. UV-Vis spectra showed reduction in intensity and decrease in width of SPR peaks as a result to annealing. Blueshift in SPR position has been observed for both heat treated films.

Keywords: Nanoparticles, Optical properties, Annealing.

دراسة الشكل السطحي و الخصائص البصرية لجسيمات الذهب-٤ ميثيلبينزنثايول النانوية مع التلدين

رجاء رشيد عباس

فرع الفسلجة و الفيزياء الطبية / كلية الطب / جامعة الكوفة

الخلاصة:

تم دراسة الشكل السطحي و الخصائص البصرية بدلالة رنين البلازمون السطحي (SPR) لجسيمات الذهب-٤ ميثيلبينزنثايول النانوية بأستخدام تقنية Langmuir-Schaefer (LS). اغشية نانوية بسمك ١ و ٣ طبقات تم تحضيرها بتركيز ١ ملغم\مل . تم تلدين اغشية جسيمات الذهب النانوية بدرجة حرارة ٢٠٠^{o}س و لمدة ١ ساعة. تم فحص الشكل السطحي للغشاء و SPR قبل و بعد التلدين بواسطة مجهر القوة الذرية (AFM) و مطياف UV-Vis على التوالي. بعد التلدين، يظهر تغير سريع في شكل و حجم الجسيمات النانوية، على كل حال، لم يلاحظ اي تأثير مهم من قبل سمك الغشاء على حجم جسيمة الذهب النانوية. اطياف UV-Vis اظهرت انخفاض في الشدة و صغر في عرض قمم ال SPR كنتيجة للتلدين. ازاحة-زرقاء في موقع SPR تم ملاحظتها لكلا الغشاءين المعاملين حرارياً.

الكلمات المفتاحية: جسيمات نانوية، خواص بصرية، تلدين.

1. Introduction

Nowadays gold nanoparticles that have functionalized with different organic ligands have attracted more interest due to their special characteristics and unique optical, electrical and magnetic properties. Due to their optical properties they have potential to be used in many applications such as labels and sensors industry, optoelectronics and medicine [1-4].

Optical properties of gold nanoparticles are arising from their interaction, at specific wavelength (frequency), between incident light and electrons on the gold nanoparticles surface. This phenomenon is called as Surface Plasmon Resonance (SPR) [5, 6]. The specific wavelength (where SPR occurs) is highly dependent on size, shape, surface morphology and agglomeration of the nanoparticles [7-10]. To improve and alter the optical properties of gold nanoparticles to be suitable in optical sensors applications where the shift of SPR peak is used as an indication to the presence of analyte molecules [11, 12], thermal annealing represents an effective method to apply [13-15]. However, studies on effect of heat treatment on the structure morphology and optical properties of gold nanoparticles under different conditions are needed.

Many publications have reported that annealing caused a drastically changes in the particle size, morphology and absorption peak intensity (and/or position) of Au NPs [16-20]. Masayuki Inuta et al [21] have noticed that annealing of 3-layers of LBL assembly of AuNPs at 300^{o}C for 1h formed raspberry-like morphology and shifted the SPR position toward lower wavelengths. Also, Jean-Claude Tinguely et al [22] have observed that there are reduction in surface roughness and increase in the AuNPs size when an electron beam lithography (EBL) gold nanoparticles have annealed at 200^{o}C. Furthermore, in our previous work on gold nanoparticles, the effect of annealing time on surface structure and SPR peak was studied with multilayers of Au-dodecanethiol NPs LS films; improvement and blue shift in SPR position were observed when annealing condition were at 220^{o}C for 1h [23]. However, study of the heat treatment on the optical properties and morphology of gold 4-Methylbenzenthiol nanoparticles has few publications.

Though, in this work the changes in the optical properties in term of SPR and surface morphology of 1 and 3-layers of 4-methylbenzenthiol functionalized gold nanoparticles (with 4nm in diameter) Langmuir-Schaefer films that annealed at 200^{o}C for 1h have been studied. The changes in the SPR peak and films surface were investigated in term of UV-Vis spectrophotometer and tapping mode Atomic force Microscopy (AFM) respectively.

2. Experimental Procedure

2.1 Material

Gold nanoparticles surrounded by a 4-methylbenzenthiol shell (Au-4MBT NPs) were sourced from PlasmaChem GmbH, Germany [24] with 4nm in diameter was used in this work. Hexamethyldisilazane (HMDS) was purchased from Sigma-Aldrich. Chloroform ($CHCl_3$) and isopropanol (IPA) were obtained from Fisher Scientific. Figure 1 represents the chemical structure of (Au-4MBT) NPs.

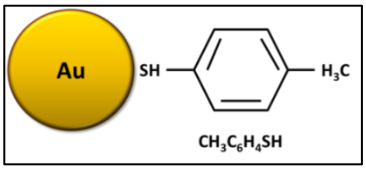

Fig. 1: Chemical structure of the Au-4Methylbenzen NPs.

2.2 Film preparation

Languimer-Schafer (LS) films with 1 and 3-layers of Au-4Methylbenzen NPs on a glass substrate have been prepared using a computer-controlled trough (NIMA; Type: 611). After cleaning the trough with chloroform and isopropanol, it filled with water; a monolayer of (Au-4MBT NPs/chloroform) solution with 1mg/ml in concentration was spread on the surface of water. The floating monolayer was compressed with 20 cm^2/min speed and the isotherm graph was recorded. The monolayer of Au NPs was found to be stable at surface pressure about 15 mN/m and therefore it was selected for preparation LS films. The 3-layers of Au NPs LS film was prepared by repeating the above procedures three times.

Heat treatment has been applied on AuNPs LS films in air using digital furnace (LINAM: TMS94) at temperature 200^{o}C for 1h with heating rate 10^{o}C/min. The annealed films have been left to cool down to room temperature inside the furnace.

2.3 Investigation measurements

Optical absorption measurements of Au-4MBT NPs LS films were carried out on a UV-Vis spectrophotometer (Helios Alpha Unicam Spectro-photometer) at room temperature. The measurements have been obtained before and after heat treatment for 1 and 3-layers of gold NPs. The wavelength range of the absorbance measurements were made over (300–1000 nm).

The morphology characterization of NPs films were performed in air at room temperature by using Tapping mode AFM (Digital Multimode AFM) with Gwyddion software.

3. Result and Discussion:

3.1 Isotherm curve

Pressure-area (π-A) graph of 100 μl of 4-methylbenzenth capped Au NPs solution with 1mg/ml in concentration is represented in Fig. 2. It can be seen that the collapsing pressure ≈ 44 mN/m for the monolayer of AuNPs LS films when the area trough is about 75cm^2.

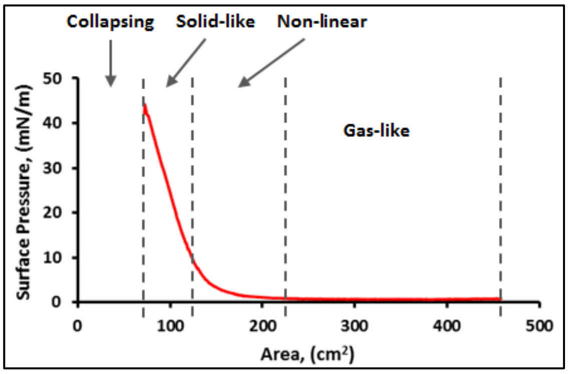

Fig. 2: ISO curve of Au-4Methylbenzen NPs

From Fig. 2, it can be noted that the isotherm graph is divided into four parts; gas-like phase where is no change in the surface pressure due to the large area of the trough and no interaction between nanoparticles, non-linear increase in surface pressure where is the nanoparticles start to interact with each other, solid-like phase where linear increase in surface pressure indicate to decreasing the spaces between the nanoparticles and formation of a monolayer film of the gold nanoparticles and finally, collapsing region where the monolayer film will break up due to overlapping of nanoparticles on each other.

For classic monolayer Langmuir nano-film, solid-like phase is chosen to deposit the film onto solid substrate where the nanoparticles locate in a close packed to form a monolayer nanoparticle film. However, the value of the surface pressure that depended to prepare the LS films that used in this work was 15mN/m.

3.2 AFM analysis

The morphology of Au-4MBT nanoparticles LS films before and after annealing were analysed by tapping mode AFM. Fig. 3a shows AFM image of the as deposited monolayer Au NPs. The film appears to be flat with some defects and many nanoclusters distributed uniformly on the film with root-mean-square (rms) surface roughness to be about 1.5nm. The formation of these nanoclusters may be due to damage of some thiols that surrounded gold nanoparticles during deposition process which lead to aggregate them with each other [25].

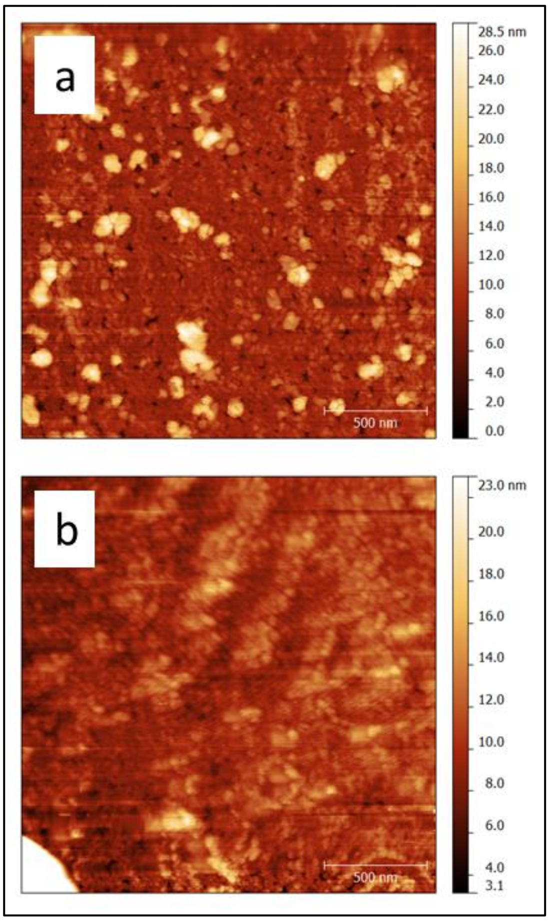

Fig. 3: AFM images of as deposited Au-4MBT NPs LS films: (a) 1-layer and (b) 3-layers. The scan size of the image is 2µm×2µm. Scale bar 500nm

Fig. 3b is an AFM image of the as deposited 3-layers Au NPs LS film. It can be seen that there is inhomogeneous in the surface distribution of deposited nanoparticles. This behavior can be explained as following: Existing of some defects and aggregations in the first layer leads to non-uniformly deposition of the next layers (second and third ones); some of the Au NPs will try to fill the holes and valleys that created previously and the rest will deposit but non-uniformly on the film surface. The measured (rms) of surface roughness of 3-layers film was 0.6nm.

Annealing effect at 200^{o}C for 1h on the surface morphology of gold nanoparticles is displayed in Fig. 4. AFM image of annealed 1-layer film (Fig. 4a) revealed a homogenous distribution of large semi spherical nanoparticles with about 50nm in size as a result to the coalescence of Au NPs during annealing process. For the annealed 3-layers film (Fig. 4b), the same trend in the morphology structure was observed but with less homogeneous in the surface height as a result to increase the number of layers that deposited on the each other.

Furthermore, one can see from the line profile of both thicknesses in Fig. 4 that the gold nanoparticles transformed to semispherical shape with average nanoparticle size approximately equal to that in the annealed monolayer film. However, the increase in the number of deposited layers did not affect significantly the resulted nanoparticle size after annealing.

3.3 UV-vis measurements

1 and 3-layers of Au-4MBT films were deposited onto glass substrate by LS technique and their UV-Vis absorption spectra before and after heat treatment were measured. The optical spectra of 1

and 3-layers of Au-4MBT NPs are displayed in Fig.5. It is clear, in general, that both films have wide peak in the range of between 550 and 610nm. However, by calculating the intensity height of the two films it will be found that the intensity of 3-Layers film about three times of that of the monolayer one which indicates that the intensity is directly proportional with film's thickness and the deposition process was achieved successfully.

It is clear from the absorption spectra that there is a small shift toward higher wavelengths as the number of deposited layers increase, where the position of SPR is about 589nm and 606nm for 1 and 3-layers as deposited LS films respectively. These results in a good agreement with that noticed by Hardy [26] where the peak of absorbance of the multilayers of Au-4MBT NPs LS films was around 590nm. The redshift with increasing film's thickness may be due to the accumulative aggregation that may occur during deposition process of the second and third layer of nanoparticles and as a result there will be an additional interactions between AuNPs located in adjacent layers [27].

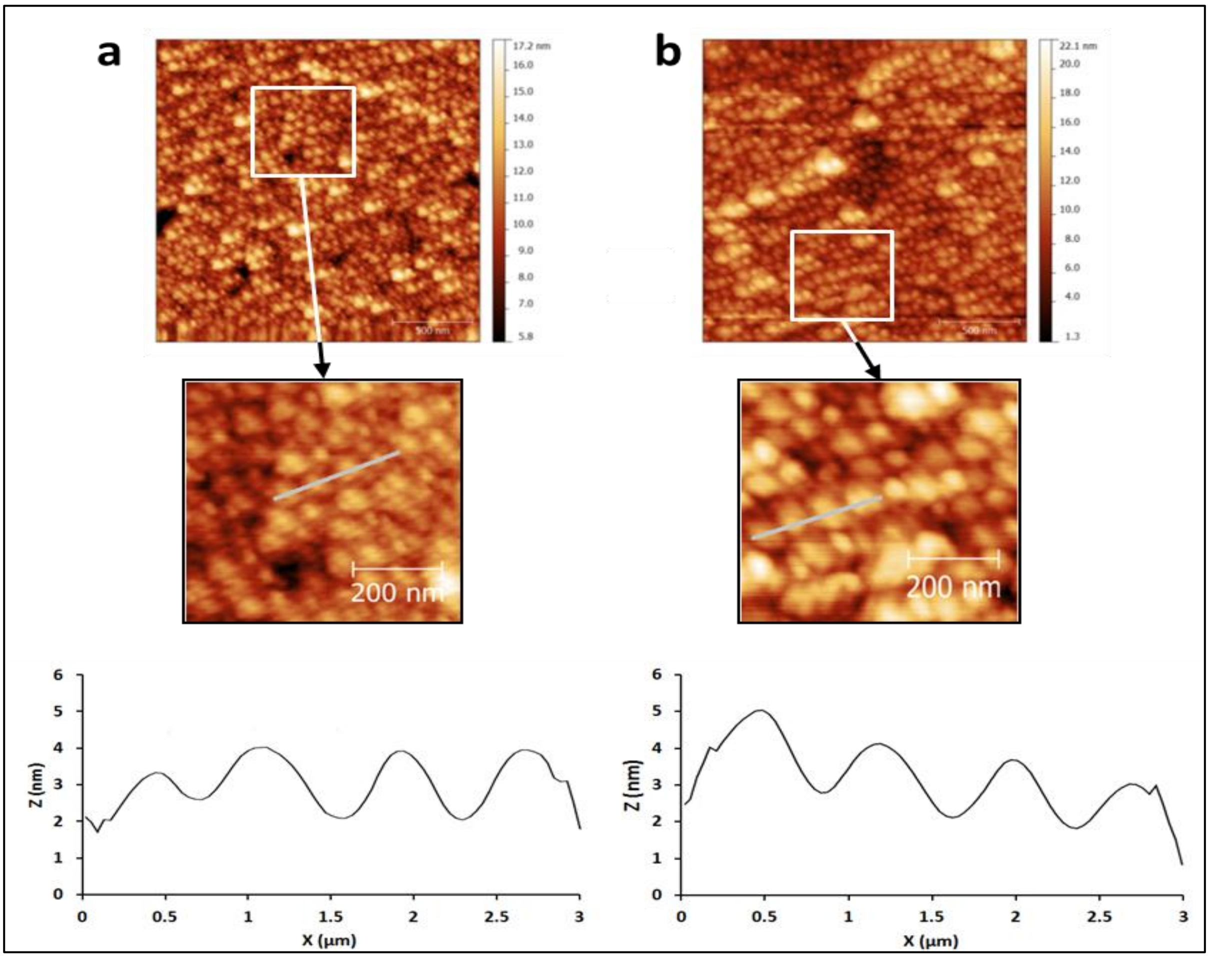

Fig. 4: AFM (2μm×2μm) images and height profile of annealed Au-4MBT NPs LS films: (a) 1-layer and (b) 3-layers

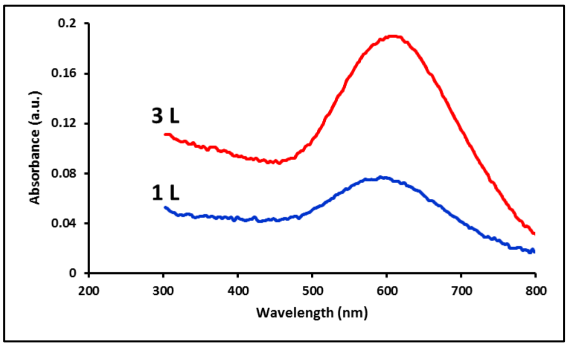

Fig. 5: UV-Vis spectra of 1 and 3-layers of as deposited Au-4MBT NPs LS films

Effect of heat treatment at 200°C for 1h on the absorption spectra of gold nanoparticles films is shown in Fig. 6. From the first sight, one can notice that SPR peaks of both thermally treated films (1 and 3-layers) have become lower in intensity and more sharpness. The reduction in intensity of the absorption peaks of annealed films in both thicknesses (1 and 3-layers) in comparison with that of as deposited one may be attributed to the not completely rounded spherical shape of nanoclusters after annealing (as displayed in Fig. 7) and non-homogeneity structure of deposited gold layers. However, the sharpness that appeared in the SPR curves after annealing indicates to the particle size distribution which became smaller after heat treatment which is in agreement with AFM results in Fig. 4.

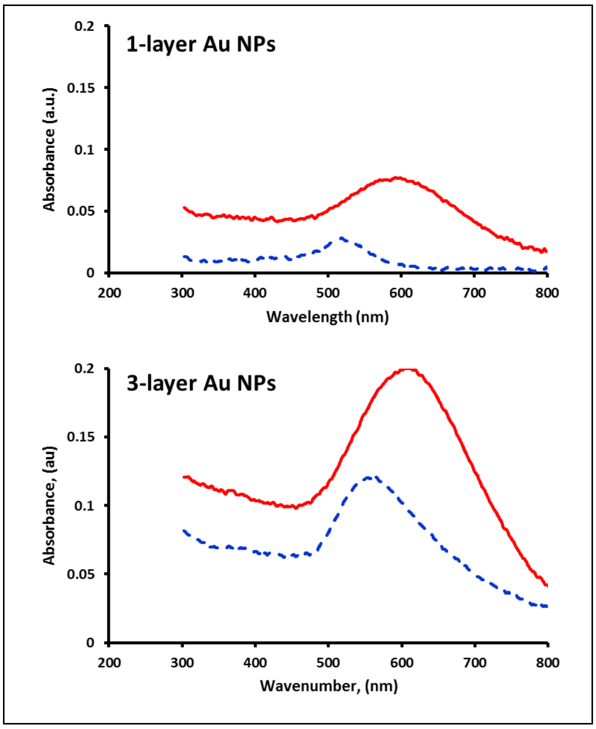

Fig. 6: Effect of annealing on the UV-Vis spectra of Au-4MBT NPs LS films before (solid line) and after (dotted line) annealing.

Furthermore, there is a shift in SPR position of both annealed films toward shorter wavelengths; from 589nm to 515nm (blue shift = 74nm) and from 606nm to 559nm (blue shift = 47nm) of 1 and 3-layers respectively. However, the blue shift that appeared in the annealed monolayer film was larger than that in the case of 3-layers one. These shifts and the difference in the values of them can be explained in term of inter-distance between gold nanoparticles.

It has been reported that the blue shift in the SPR position is due to increase in the distances between nanoparticles which cause a reduction in the dipolar interaction between adjacent particles [13]. In the case of monolayer film, annealing leads to partial fusion and coalescence of individual nanoparticles into nanoclusters and as a result the distances between them will be bigger; consequently the SPR peak will shift to smaller wavelengths. In the case of 3-layers annealed film, the same mechanism will happen but because the gold nanoparticles mass is larger than that in the monolayer one, the distances between the nanoclusters are decrease (as seen clearly in 3D AFM topographic images of AuNPs LS film before and after annealing, Fig. 7) which lead the blue shift to be smaller. The same behavior has been observed in Refs. [15, 17].

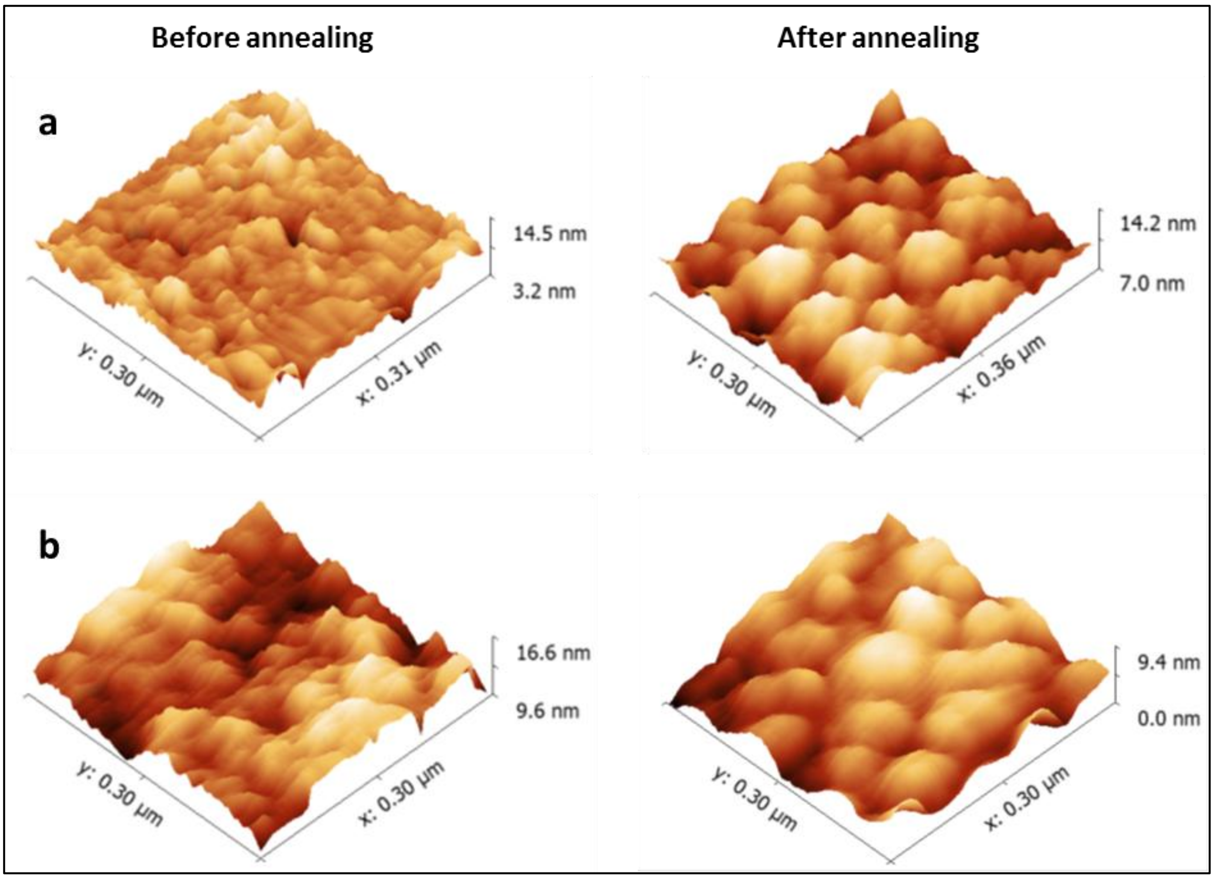

Fig. 7: 3D AFM topography images of (a) 1-layer and (b) 3-layers Au-4MBT NPs before and after annealing

4. Conclusions

The changes in the surface morphology and SPR of 1 and 3-layers of 4-methybenzenthiol capped gold nanoparticles Langmuir-Schaefer (LS) films as a result to annealing at 200^{o}C for 1h have been studied. AFM images results revealed that the number of layers does not affect the nanoparticle size after annealing.

Heat treatment was affected position, width and height of the SPR peak. The UV-Vis spectra, for both thicknesses, have become more sharpness and lower in intensity after annealing. The blueshift in SPR position may attribute to distances between nanoclusters that have formed as a result to thermally treatment.

However, heat treatment represents a good and simple method for tunning SPR of gold nanoparticles to be suitable in toxic gases sensing applications.

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