Surface Plasmon Resonance study of Ag nanoparticles colloidal

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Abstract

Silver nanoparticles (Ag-NPs) have been prepared using the electro-chemical method. The experimental setup of this technique consist of two electrodes of pure silver (99.2 %), the applied voltage on the electrodes is 20 V and the current through the colloidal was about 0.4 Amp. The silver nanoparticles crystallization has been studied; the crystalline structure appears Face center Cubic. The optical properties of silver nanoparticles are strongly affected by the Local Surface Plasmon Resonance (LSPR)**.** The wavelength of maximum absorption band for an Ag NPs have a range (~350nm-550nm).

Keywords: Ag nanoparticle, electrochemical method, surface Plasmon resonance, EDX test.

دراسة رنين بلازمون السطح لسائل الفضة الجسيمات النانوية الغروية

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الخلاصة

تم تحضير الجسيمات الفضة النانوية باستخدام الطريقة الكهروكيميائية. الإعداد العملي لهذه التقنية يتكون من قطبين من الفضة النقية (99,2%)، والفولتية المسلطة على القطبين 20 فولت والتيار المار خلال الغراء بحدود (0,4 امبير). وقد تمت دراسة تبلور جسيمات الفضة النانوية ، ويظهر التركيب البلوري مكعب متمركز الوجه. الخصائص البصرية لجسيمات الفضة النانوية تتأثر بقوة بالرنين الموضعي لبلازمون السطح ،والطول الموجي لأقصى امتصاص لجسيمات الفضة النانوية يقع ضمن المدى (350−550   ) نانومتر.

Introduction

In the last twenty years, metal nanoparticles have been the subject of focused research due to their distinguished contribution that is significantly possibility from those of bulk complement. Proper to their small size, nanoparticles have a high surface to volume ratio, this increases the surface energy compared with that of bulk materials. The high surface to volume ratio together with the size effect gives nanoparticles discriminative different properties (chemical, optical, electronic and magnetic) from those of bulk material [1-5]. Different preparation methods have been reported for the preparation of metal oxide nanoparticle, notable examples comprise, laser ablation, gamma irradiation , electron irradiation , chemical reduction , photochemical methods, microwave processing, and biological synthetic methods [6]. These days, silver Nanoparticles have gained tremendous attractiveness in the world in the field of sensors because of outstanding importance optical, electronic

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and chemical properties [7-9]. Silver nanoparticles exhibit new optical properties, which are observed neither in molecules nor in bulk metals. An example is the presence of absorption band in the visible light region. The silver nanoparticles have their conduction band and valance band very close to each other, allowing the electrons to move freely. These free electrons give rise to a surface Plasmon resonance (SPR) absorption band, occurring due to the collective oscillation of electrons of silver nanoparticles in resonance with the light wave. When the frequency of the electromagnetic field becomes resonant with the coherent electron motion, a strong absorption takes place, which is the origin of the observed color [10-13]. Among all the metals, Silver exhibits the highest electrical and thermal conductivities [14]. In this work silver nanoparticles were prepared by electro-chemical technique. The effect of time preparing of Ag nanoparticles on the surface Plasmon resonance was studied.

Experimental Work

The proposed process for obtaining silver nanoparticles is based on the use of two plates of pure silver (99%) has dimensions of (60mm high, 25 mm wide, 1 mm thick), were immersed inside the beaker. The electrochemical method involved a 250ml beaker filled with distilled water, the two silver electrodes oriented vertically and placed face to face with about 1cm separation distance. Stage I: a potential of 20 volts was applied to the electrode and the polarity of the direct current was changed every 5 minutes to prevent the black layer of silver oxide depositing on the cathode due to the gradual reduction of the efficiency of the surface pole [14]. The distilled water was heated (from 50 ^{0}C to 60 ^{0}C) to release the oxygen from the water. Figure-1 shows the process of formation of colloidal silver nanoparticles in the electrochemical method, and Figure-2 shows the photographic image of the experimental setup. Stage II: additional treatment, the prepared silver nanoparticles has a stable particle size due to the use of the hydrogen peroxide (H_2O_2) stabilizer, leading to a reduction the particle size of the silver nanoparticles and avoidance of silver oxide Ag_2O due to the reaction:

$Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$

This treatment includes adding hydrogen peroxide at a concentration of 0.005 %. Due to this process, the size of the silver nanoparticles is reduced while new Ag nanoparticles may be forming as well.The details of this process, whose outcome consists of in a significant refinement of the nanoparticle size, are not fully understood as yet [15]. Added amount of H_2O_2 to the Ag colloidal is 5ml. The PVP (poly Nvinyl pyrrolidone) was used as a protective medium for the silver nanoparticles colloidal suspension.
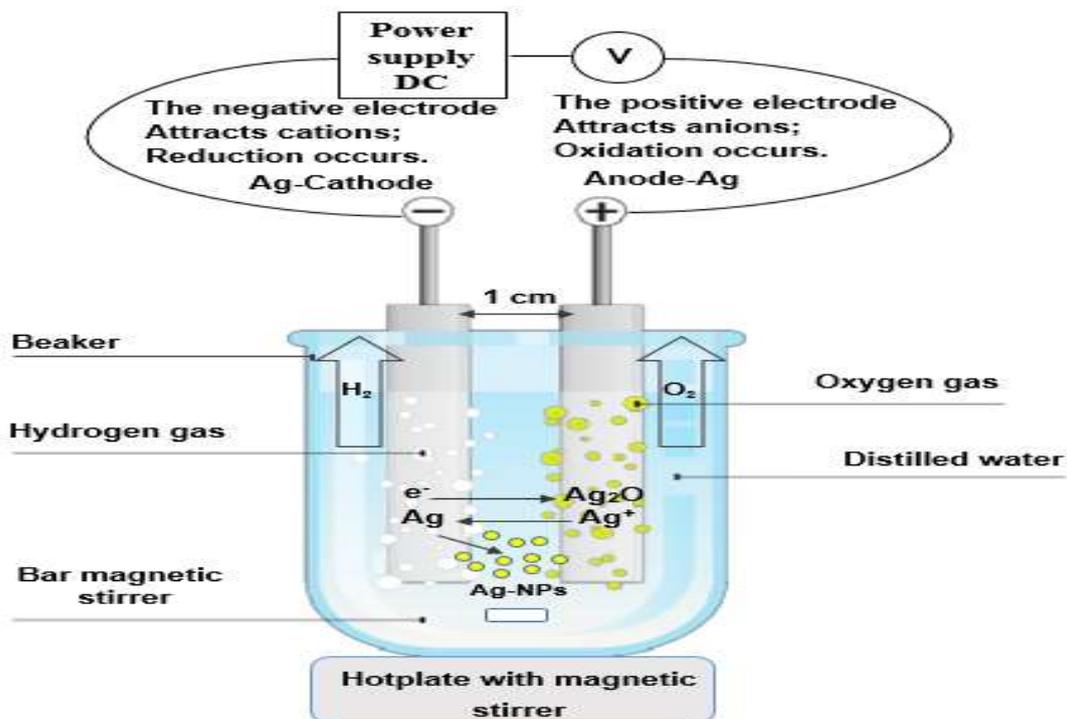
Figure 1-Illustrates scheme of the formation of silver nanoparticles by electrochemical method.
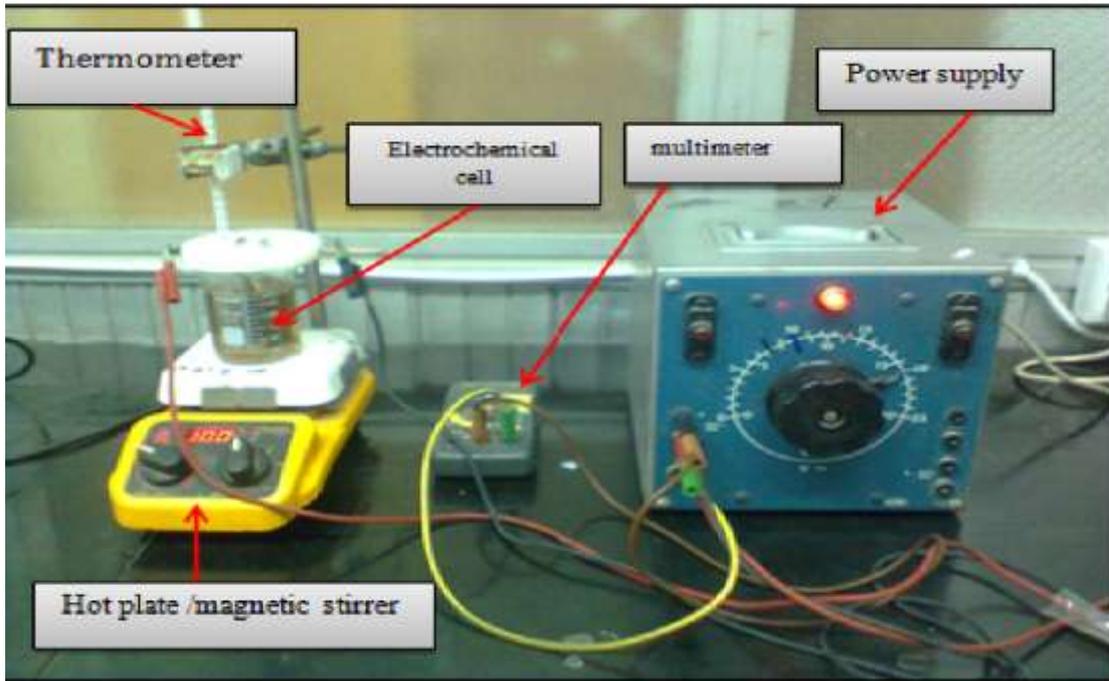
Figure 2- The Experimental Setup.

Result and Discussion
X – Ray diffraction study

The technique which used in this work to study crystallites structure of the Ag nanoparticles thin film deposited on a glass substrate (by the drop casting method) is an X–ray diffraction spectrum method. This technique used (XRD -6000 labs, supplied by SHIMADZU, X-ray source are Cu Kα). The X-ray is used to determine the dimensional parameters for crystals and estimate the particle size. For this purpose the following equation, known as the Scherrer equation is used [16]:

$$D = \frac{K\lambda}{\beta \cos\theta}$$ ....(1)

where K is the shape factor, the dimensionless shape factor has typical value 0.9. D is the particle size. λ is the wavelength for X-ray source (X-ray source is CuKα with λ=1.5406Å). β is the full width at half maximum (FWHM) in rad. θ is the diffraction angle. The Ag NPs have a cubic polycrystalline structure with peak positions illustrated in Figure-3, which agree with the standard data get from PCPDFWIN (card no. 7440-22-4).
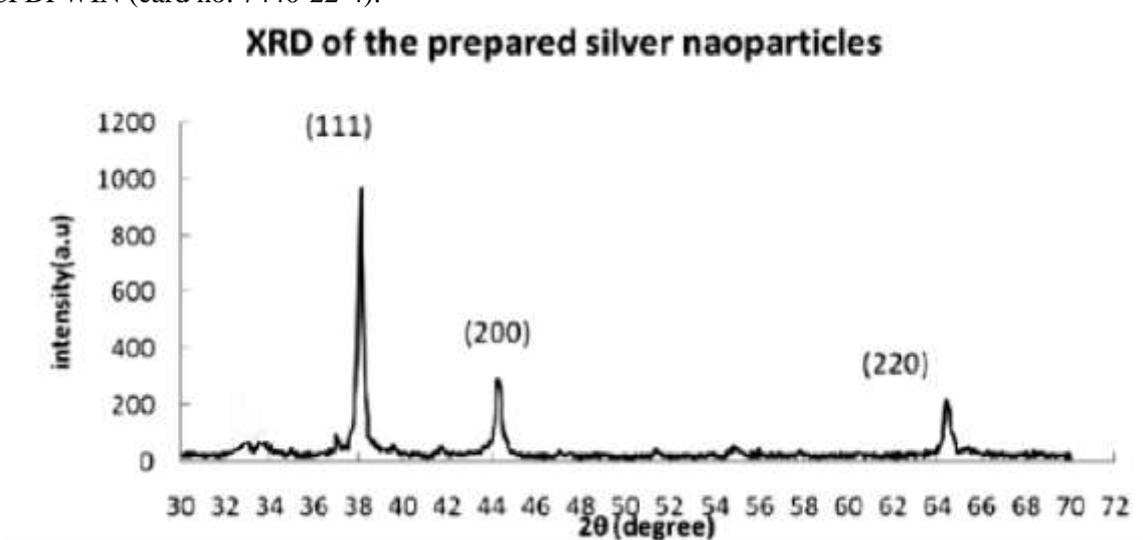

**Figure 3-** The XRD Pattern of Ag Nanoparticles.

The Bragg`s angle (2θ) at $38^0, 44^0, 64^0$ had the reflection planes (111), (200), (220) respectively, which indicate that we have a polycrystalline structure with the Face-centered Cubic phase (F.C.C.) structure. The X-ray peaks and their bandwidths are illustrated in Table (1) and the corresponding grain size of the prepared nanoparticles calculated according to the Scherrer equation (1). Eventually the average value of the diameter of Ag NPs is (22 nm) which indicates that the formation structures are of nano-dimension.

Table 1-The Grain Size of The Prepared Ag Nanoparticles as Estimated Via the Scherrer Formula.

2Theta(degree)	Cos θ	FWHM (degree)	Grain size (D) nm	(hkl)
38^0	0.987	0.24	33.9	(111)
44^0	0.927	0.48	17.26	(200)
64^0	0.848	0.56	16.925	(220)

UV-Visible spectroscopy

The UV-vis absorption spectrum of the prepared Ag NPs is measured using Shimadzu UV-1800 spectrophotometer, covering a range from (190-1100) nm. The scanning range of the Ag nanoparticles absorption was (300-900) nm using distilled water for Ag NPs as a reference sample. Figure-4 shows the UV-Visible absorption spectra of Ag nanoparticles colloidal as a function of wavelength.
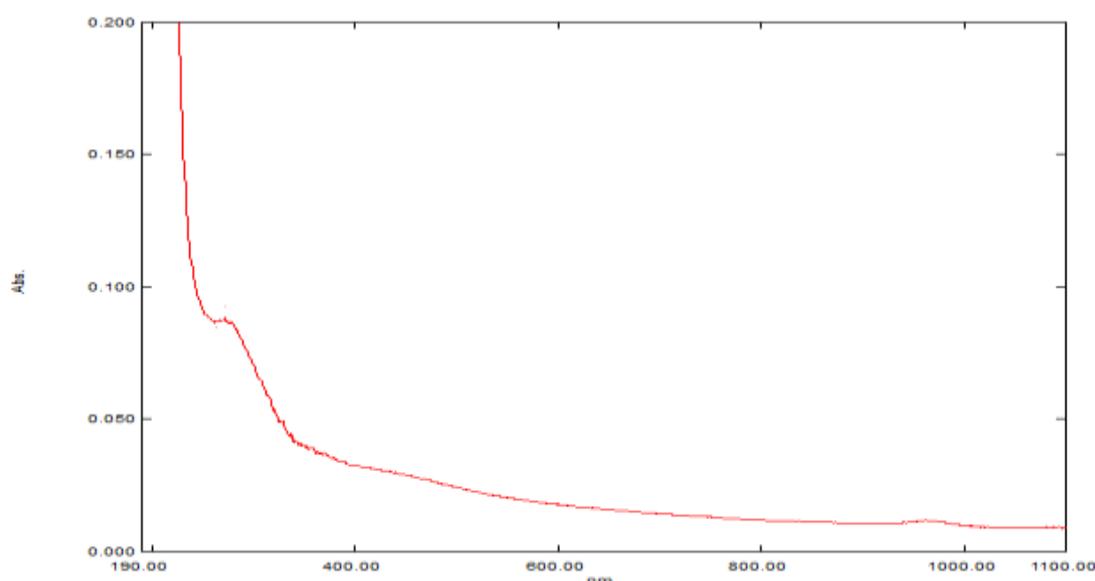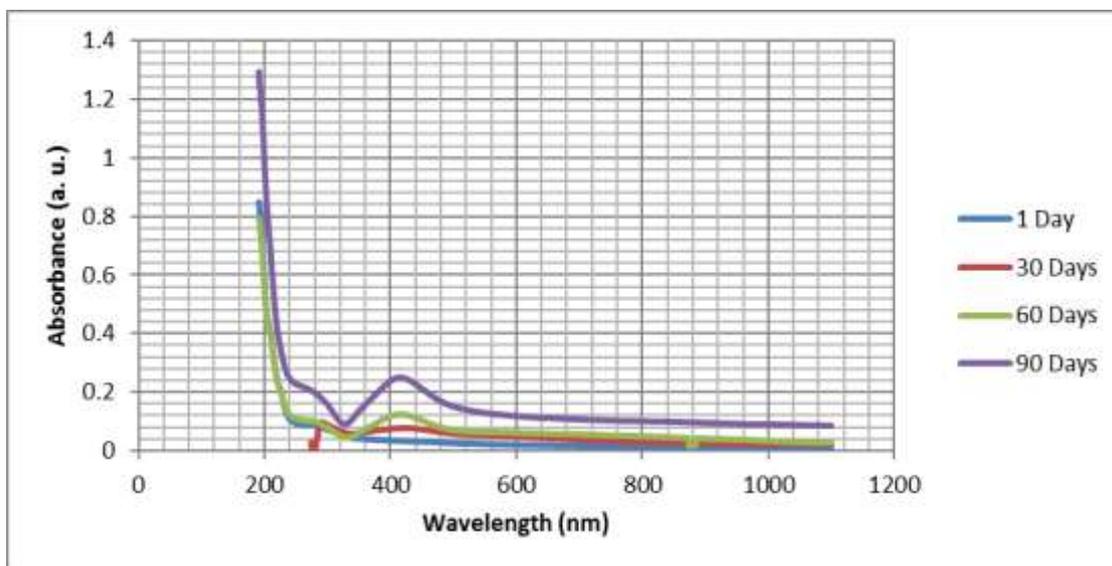

Figure 4- Absorption spectra of Ag nanoparticle colloidal as a function of wavelength.

Surface Plasmon Resonance (SPR) analyses

The optical properties of silver nanoparticles are strongly affected by the Local Surface Plasmon Resonance (LSPR) The wavelength of maximum absorption for an Ag NPs peak have range (~350 nm to 550 nm). The color of the prepared silver nanoparticles is yellow .This absorption strongly depends on the particle size, dielectric medium and chemical surroundings. Since the small spherical nanoparticles less than 20 nm exhibit a single surface Plasmon band, the UV-Visible absorption spectra of Ag NPs in Figure-5 shows a knee in the UV region at 272nm after 1 day from the synthesis of Ag NPs as shown in Figure-4. But after 30 days this flat, broadband was narrower due to the increase of Ag NPs size on the colloidal lead to small absorption peak in the visible range of 424 nm, as shown in the inserted part in Figure-5. The UV-Visible absorption spectra of Ag NPs samples after 60 days show that the absorption peak is at the wavelength of 417 nm, and after 90 days absorption

peak is shown at the wavelength 416. Table-2 shows the change in the particle size with wavelength for the Ag colloidal after different time period, which calculated from FWHM of SPR absorption band. The resultant color of the prepared Ag colloidal changes from clear to yellow in different stages of reaction and treatment, due to the enhancement in the single surface Plasmon resonance, the colors change of Ag colloidal after different time period are shown in Figure-6. The yellow color of the colloidal continues for long periods of time due to the protective layer PVP molecules adhere to the surface of nanoparticles, and is an indication for the formation of Ag NPs colloidal.

**Figure 5-** Absorption peaks of Ag NPs after different time period.

Figure 6-The silver nanoparticles for different periods.

Table 2- shows the change in the particle size with wavelength calculated from the UV-visible spectrum.

Time period (Day)	Wavelength of peak absorbent (nm)	Particle size of Ag NPs (nm)
30	424	4.4
60	417	5
90	416	5.7

**Energy Dispersion X-ray (EDX) Analyses**

Analysis of Energy Dispersive X-rays (EDX) performed by using Bruker Nano GmbH, Germany SEM. The EDX gives a real approved forming the Ag NPs in the colloidal, as shown in Figure-7 with concentration reach 1.6mg per 200ml.
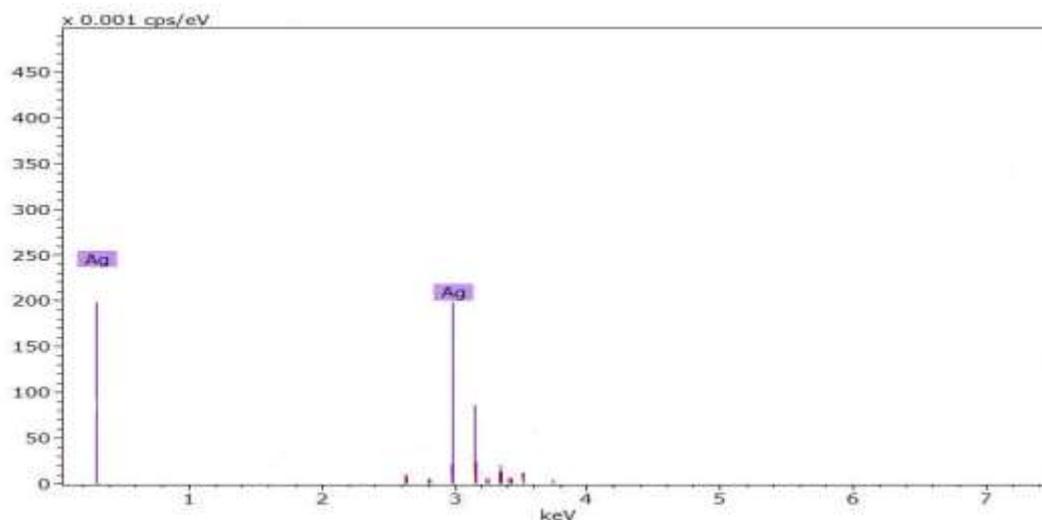
Figure 7- The EDX Analysis of Ag Colloidal.

Atomic Force Microscope (AFM)

The surface morphology and nanoparticles average dimensions of the samples are studied by using Atomic Force Microscopy CSPM AA3000 AFM supply by Angstrom Company. The prepared Ag NPs were analyzed using AFM. Picture shown in Figure-8(a) is for the morphology of the Ag NPs, while Figure-8(b) is for the calculated average diameter of the Ag NPs, the measured average diameter using the software of the AFM is 86.57 nm, and it seems that the Ag NPs had homogenous distribution with small cluster as shown in Figure-8(a).
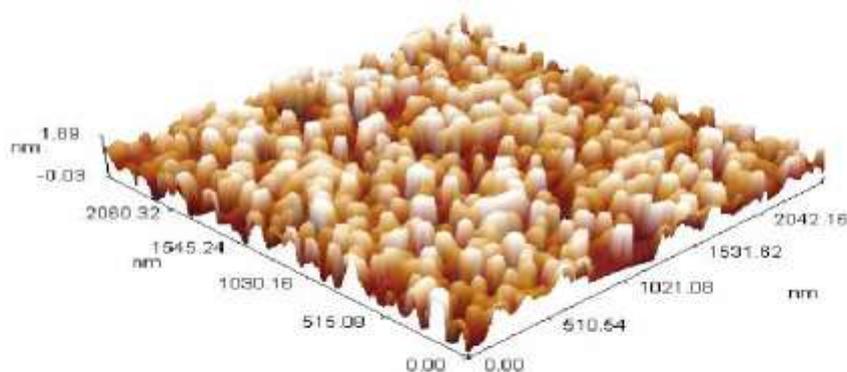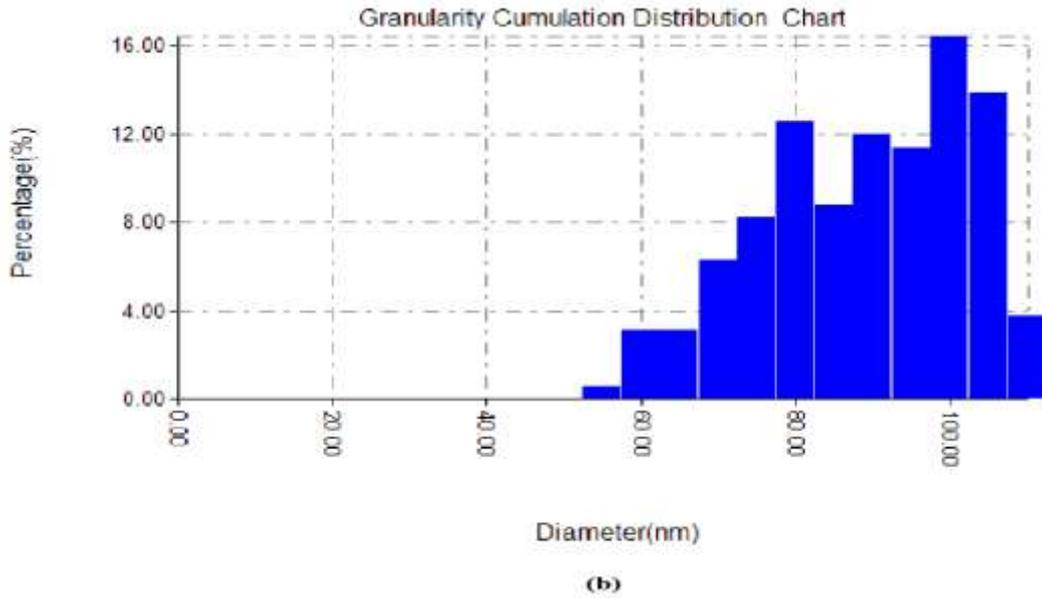

(a)

Figure 8(a)- The AFM of Ag NPs, **(b)** Ag NPs distribution chart.

Scanning Electron Microscope (SEM)

Scanning Electron Microscope studies were used to determine the nanoparticles distribution, nanoparticles size, show the structure and shape of nanocrystal using VEGA3 TESCAN, mode SE from TESCAN ORSAY HOLDING, a.s., Czech Republic, where high-resolution images of the surface of a sample is acquired. The SEM image of Ag NPs shows the spherical clustered and the luminous of Ag NPs as shown in Figure-9(a). while Figure-9(b) shows the polymer capped the Ag NPs.
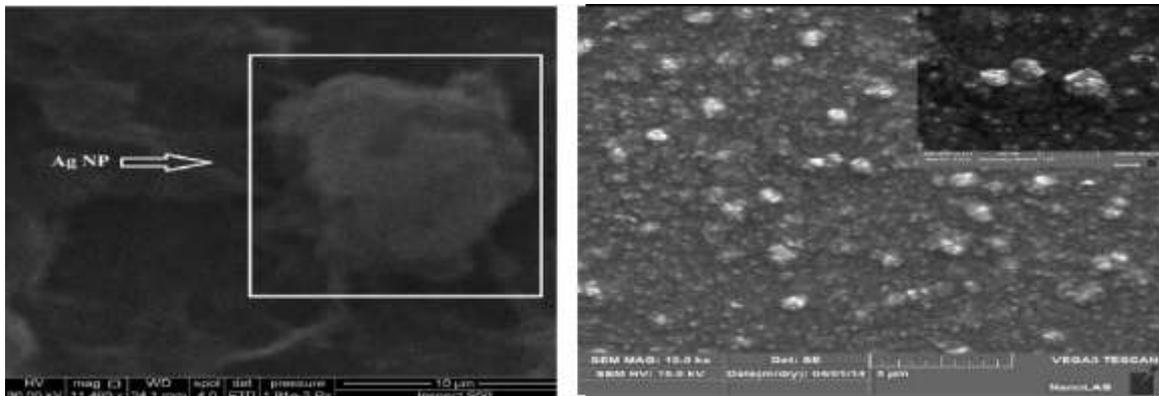

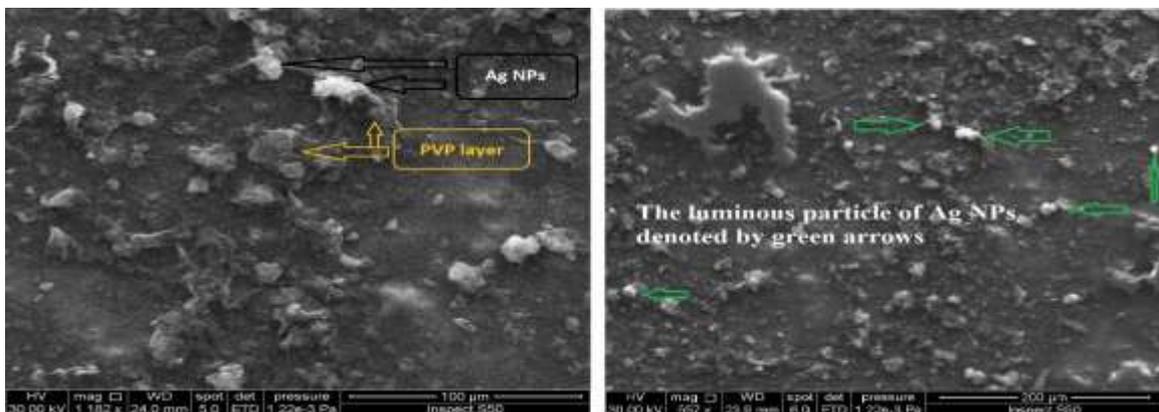**Figure 9(a)-** spherical clustered of the Ag NPs film.

Figure 9(b)- shows the polymer capped the Ag NPs.

Conclusion

The electrochemical method can be recommended to prepare the silver nanoparticles due to the simplicity of this synthesis route allows, low cost fabrication of large amounts of long –lived silver nanoparticles without chemical tabling agents. From SEM study, it is found that Ag nanoparticles are of spherical shape capping by PVP. The SPR study after 30, 60, and 90 days shows the enhancement of colloidal, which changed from pale yellow to strong yellow.

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