

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Growth of Silver Nanoparticles Using Gamma Irradiation and Polyvinylpyrrolidone

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ABSTRACT

Well-dispersed silver nanoparticles (Ag NPs) were prepared via two different pathways within PVA matrix. Gamma irradiation and polyvinylpyrrolidone (PVP) induce the growth of the Ag NPs. TEM study shape, The X-ray diffraction (XRD) confirm the crystallinity nature of the as-prepared Ag NPs. UV-visible spectra show a narrow and intense absorption surface plasmon resonance (SPR) which implies a monodispersed Ag NPs were obtained via these methods. Mechanisms of gamma and PVP in the preparation process were discussed through the FTIR of the reaction system.

Keywords: Ag NPs; γ -irradiation; PVP; UV-visible; FTIR

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INTRODUCTION

Unique optical, electrical and excellent catalytic properties of metal nanoparticles have spurred interest in developing different synthetic methodologies for diverse applications [1]. Among these, silver nanoparticles have been widely investigated depending on their size and shape. Being in nano scale, these nanoparticles have high surface: volume ratio. Therefore they often show unique and considerably different physical, chemical and biological properties compared to their macro scaled counterparts. Silver nanoparticles can also be used in various near field oxidative catalysis, surface enhanced Raman scattering, nanoelectronic, conductive coatings, biosensors, antibacterial activity, ect [2]. Ag NPs can be synthesized using various methods some of them are chemical reduction, electrochemical, reduction, photochemical, reduction-ray irradiation, UV irradiation, microwave, and ultrasonic [3]. Using of high energy radiation on synthesis of Ag NPs is being explored extensively in literature. The growth of metallic nanoparicles in solution induced by γ -ray [4, 5], electron beam [6, 7] and X-ray [8, 9] irradiation has been proved to be an alternative way to obtain dispersed nanoparticles.

The radiation method offers many advantages for the preparation of metal nanoparticles. Hydrated electron, resulted from the radiolysis of the aqueous solutions, can reduce metal ions to zero-valent metal particles, avoiding the use of additional reducing agents and the consequent side reactions [10, 11, 12]. Furthermore, the amount of zerovalent nuclei can be controlled by varying the dose of the irradiation [13].

The polyol process has been proposed as a method for the preparation of finely divided powders of easily reducible metals. A suitable solid inorganic compound is dissolved or suspended into a liquid polyol. The reduction of the starting compound yields the metal as a finely divided powder. The starting compound may be a hydroxide, oxide or a convenient salt. The main feature of the reaction mechanism is that the reduction reaction proceeds via the solution rather than the solid phase. Therefore, the metal particles are formed by nucleation and growth from solution. According to this mechanism, the polyol acts as a solvent for the starting inorganic compound due to the rather high dielectric constant of these organic media [14].

This study aims at exploring the possibility of synthesizing Ag NPs within PVA matrix using two different approaches. The first is by using γ -irradiation (chemical free reduction method) and the second are by blending with polyvinylpyrrolidone (PVP) (water soluble and a biodegradable polymer) as the reducing agent under normal atmospheric conditions. A comparative study of the size, size distribution and structure resulted from the two methods is evaluated.

EXPERIMENTAL

Preparation of the gamma irradiated PVA/Ag nanocomposites

The samples were prepared according the method described elsewhere [15]. Different volumes of 10^{-1} M AgNO_3 solution were added to 10 ml of 6% aqueous solution of PVA with continuous stirring for about 1 hr to insure well homogeneity of the solution. The pH of the solution was adjusted to 4 using 0.1 M HNO_3 to avoid the spontaneous reduction. Finally, the solution was casted on a Petri dish, left to dry in darkness to form the desired film and then the film was stripped from the dish. The as-prepared samples were subjected to gamma irradiation using a Gamma cell 220 Excel ^{60}Co irradiation facility (manufactured by MDS Nordion, Canada).

Synthesis of PVA/PVP/Ag nanocomposites

8 mL of 6% aqueous solution of PVP were added to 2 mL of 6% aqueous solution of PVA, under continuous stirring until homogeneous solutions were obtained. The pH of this mixture is adjusted using 10^{-1} M of HNO_3 . Thereafter, 0.6 ml of 5×10^{-2} M of AgNO_3 was added to the above mixtures with continuous stirring. Finally, the solutions were poured on Petri dishes, kept in dark and left to dry at ambient condition to form the desired films and then the films were stripped from the dishes. The stripped films are perfectly colorless.

Analysis techniques

The shape and particles size distribution were studied using JEOL 2010 TEM (JEOL TEM.-1230 Electron Microscope, Tokyo, Japan) imaging. The samples were prepared by making a suspension from the powder in

distilled water using an ultrasonic water bath. Then a drop of suspension was put in the carbon grid and left to dry. X-ray diffraction technique was used to determine the diffraction patterns of the crystal structure. X-ray diffractometer (Shimadzu 7000, Shimadzu Corporation, Tokyo, Japan) was used, operating with Cu K α radiation ($\lambda=0.154060$ nm) generated at 30 kV and 30 mA with a scanning rate of 4 min⁻¹ for 2h values between 20 and 90 degrees. UV-Visible spectra were measured in the range of 200 - 1000 nm using a JASCO 570 UV-Visible-NIR infrared.

RESULTS AND DISCUSSIONS

TEM

Transmission electron microscope was used to obtain direct information about the shape and size of 75 kGy gamma irradiated PVA/Ag and PVA/PVP/Ag nanocomposites.

Figures (1-2) show TEM image of Ag NPs obtained from γ - irradiation and that prepared by PVP. The Gaussian fit to the particle size histogram is performed and is shown as a solid line in each Figure. The average diameter of the nanoparticles is indicated as the peak position of Gaussian curve of the histogram. The nanoparticles are well-dispersed in the TEM picture with external spherical shape and are to a large extent well-separated from one another. The particles obtained using gamma irradiation was smaller in size as compared with those obtained with the aid of PVP.

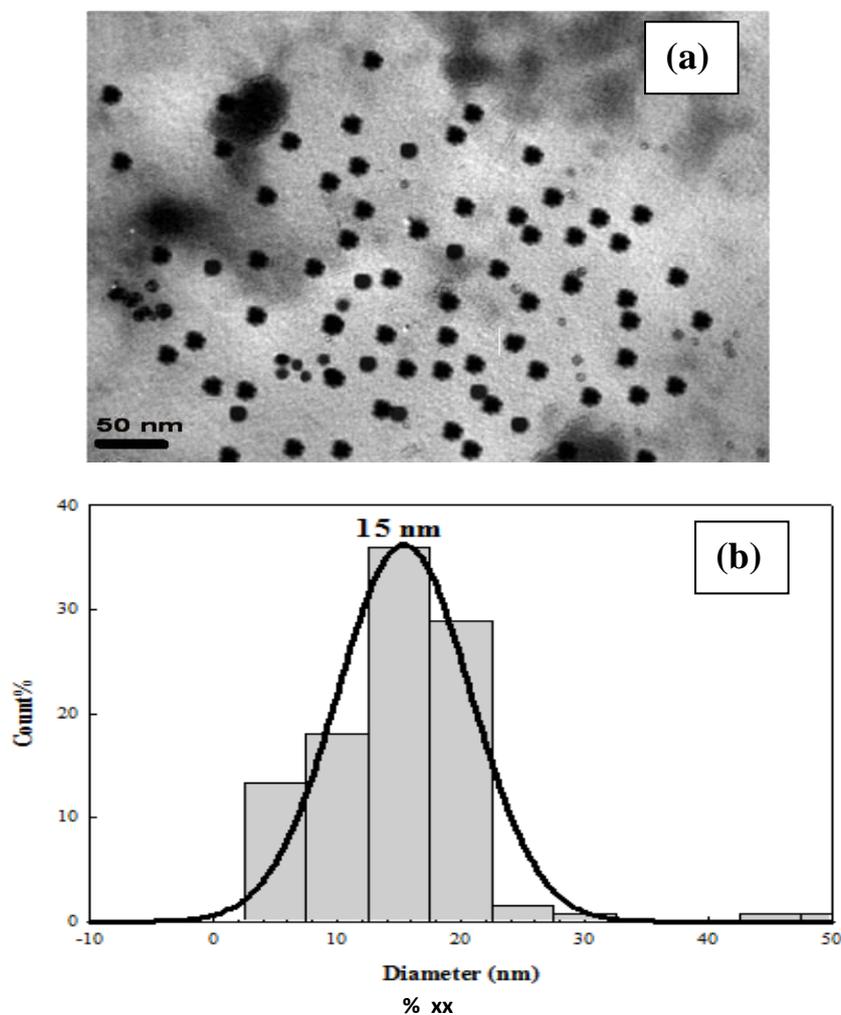


Figure 1 (a) TEM image of Ag NPs and (b) the histogram of the particle size distribution with Gaussian fitting for 75 kGy γ -irradiated PVA/Ag nanocomposite

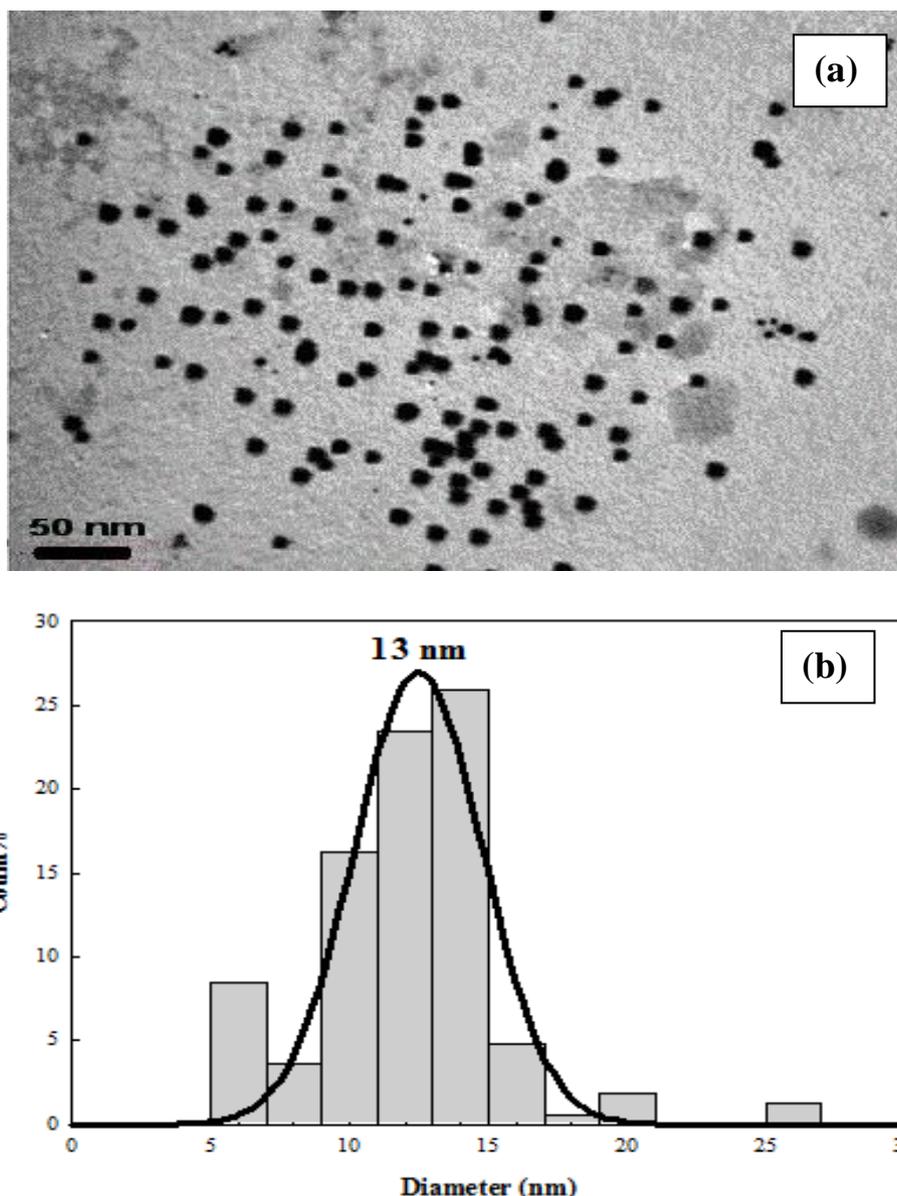


Figure 2 (a) TEM image of Ag NPs and (b) the histogram of the particle size distribution with Gaussian fitting for unirradiated PVA/PVP 50/50 filled with 5×10^{-2} AgNO₃

XRD:

The X-ray diffraction pattern for gamma irradiated PVA loaded with 5×10^{-2} of AgNO₃ is given in **Figure 3a**. The diffraction peak at $2\theta = 19.66^\circ$ corresponds to the (110) reflection from the PVA chains. The peaks for 2θ values at 38° , 44° , 64.4° and 78° are pertaining to Ag NPs which indicate the reduction of the Ag salt in the polymer matrix. The diffraction peaks can be assigned to the plans (111), (200), (220) and (311) respectively corresponds to face centred cubic structure of Ag according to JCPDS (No.4-0783).

The effect of blending with PVP on the XRD pattern of the PVA/Ag matrix is shown in **Figure 3b**. In addition to the main peak at $2\theta = 19.66^\circ$, the PVA/PVP blend exhibits an amorphous scattering peak $2\theta = 22.38^\circ$. This is the characteristic peak of the PVP film [17]. Once again, the appearance of the Ag lines confirm the role of PVP as reducing and stabilizing agent. The Ag diffraction peaks are more intense as compared with those appeared due to gamma irradiation.

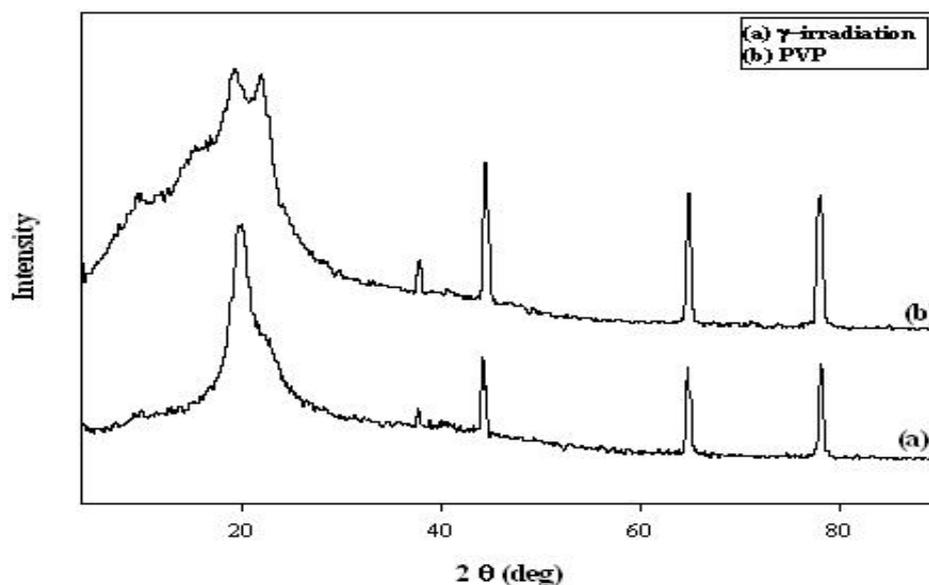


Figure 3 X-ray diffraction patterns of (a) 50 kGy gamma irradiated PVA/Ag and (b) PVA/PVP/Ag films filled with 5×10^{-2} M AgNO_3

The crystalline particle size of the as-prepared Ag nanoparticles is estimated by using Scherrer formula [18]

$$D = k\lambda / \beta \cos\theta$$

The equation uses the reference peak width at angle θ , where λ is the X-ray wavelength (1.54\AA), β is the FWHM of the XRD peak and K is a shape factor. The calculated Ag Nps were 13 nm and 11 nm corresponding to gamma irradiated and PVP blend, respectively.

UV-Visible

Reduction of silver ions was routinely monitored by visual inspection of the prepared samples. Initially, the synthesis of silver nanoparticles was confirmed by observing the color change of the reaction mixture. The appearance of a brown color suggested the formation of silver nanoparticles. Note that we have performed control experiments in order to investigate the role of nitric acid on the synthetic process. We perform the same experiments without HNO_3 under darkness. 6-8 hours after casting, the composite film (which is still not dried) shows a remarkable reddish brown color i.e. the silver salt was reduced before the drying of the polymeric film. After drying, the stripped films were of non-uniform color i.e. the resultant film consists of dark and faint regions. This observation may lead to conclude that the Ag nanoparticles were inhomogeneous distributed in the polymer matrix. Using the HNO_3 in the preparation will result in formation of colorless films after drying which indicate that the silver ions were kept un-reduced.

When PVA/ AgNO_3 films are subjected to γ irradiation, the optical properties are the net result of the electronic transition of the two materials. Fig. 4a shows the UV-visible absorption spectra of PVA filled with 5×10^{-2} M of AgNO_3 irradiated with 50 kGy gamma irradiation dose. The spectrum exhibits an intense absorption peak at 412 nm which is the surface plasmon resonance (SPR) of the Ag nanoparticles [16]. The dramatic enhancement in absorption is found to be in agreement with the color of the samples, which is turned yellowish brown after irradiation.

The UV-visible spectroscopy was used to study the effect of blending PVA/ AgNO_3 with PVP. Fig. 4b displays the electronic absorption spectra of the PVA/PVP/ AgNO_3 polymer blends containing 80% of PVP. The SPR band of Ag nanoparticles emerged at 408 nm. It is worthwhile to mention that this absorption band appears after 25 day of casting. The symmetric and narrow absorption peak implies the narrow size distribution of the silver nanoparticles at higher irradiation doses obtained by these methods

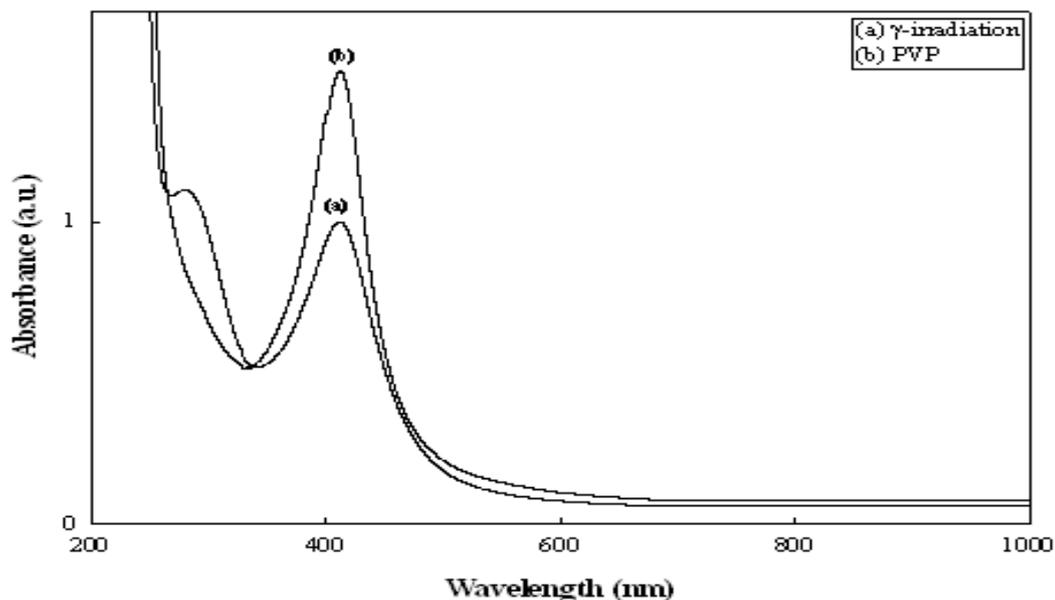


Figure 4 UV-visible absorption spectra of 75 kGy γ -irradiated PVA/Ag and unirradiated 50/50 PVA/PVP/Ag nanocomposites.

FTIR Spectroscopic Analysis:

FTIR spectroscopic analysis was used to illustrate the composition and nature of bond formation into PVA/Ag nanocomposites. The evolution of FTIR spectra of PVA, 50 kGy gamma irradiated PVA/Ag and PVA/PVP/Ag nanocomposites were displayed in **Figure 5**.

Three structural features were induced due to interaction between Ag^+ ions and PVA chains. The $-\text{OH}$ stretching band located at 3260 cm^{-1} was shifted to 3235 cm^{-1} and become to somewhat broader and weaker. It is well known that, when the metallic clusters and nanoparticles are capped by the PVA chains, two kinds of bonds may contribute to the Ag-PVA complexation, namely, Ag-C and Ag-O bonds. The rigid structure of the C-C bond in monomer unit impedes the formation of Ag-C bonds. Hence, the binding of silver clusters by PVA is likely achieved through the Ag-O bond. The complexation of silver with polymers via the Ag-O bond was also confirmed in previous reports by XPS measurement [19]. The spectral shift together with reduced intensity of the $-\text{OH}$ stretching vibration upon incorporation of the Ag nanofiller indicates to interaction between Ag nanoparticles and the OH groups originating from the PVA chains.

The IR absorption band at 1655 cm^{-1} grew at the expense of the absorption band at 1564 cm^{-1} which was found to decay markedly with increasing AgNO_3 content. The increased intensity of the $-\text{C}=\text{O}$ at 1655 cm^{-1} can be correlated to the prominent oxidative degradation reaction accompanying the reduction of Ag Nps. The disappearance of 1564 cm^{-1} absorption peak can be attributed to some sort of $-\text{C}=\text{C}-$ structure deformation and/or chain scissions of the polymer as a result of interaction with AgNO_3 . Finally, the crystallization sensitive band at 1136 cm^{-1} was reduced as the AgNO_3 content was increased reflecting the negative effect of the AgNO_3 on the crystallinity of the PVA matrix. This result is in good agreement with the results obtained from XRD results.

The FTIR spectra of different PVA/PVP blends filled with Ag Nps were displayed in **Figure 5c**. It is worthwhile to pay attention to the structural features aroused in the spectral region $1155\text{--}1000\text{ cm}^{-1}$. The C-N absorption peak at 1020 cm^{-1} was separated from the broad peak centered at 1090 cm^{-1} and shifted to the low frequency side (1004 cm^{-1}). This implies that there is weak coordinative chemical bonding of C-N to Ag Nps.

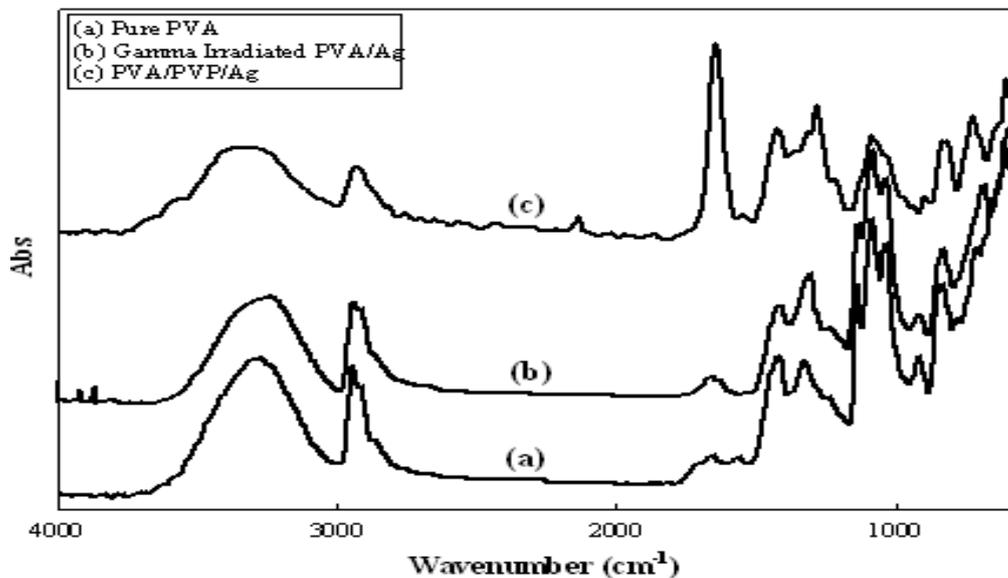


Figure 5 FTIR spectra of (a) PVA, (b) gamma irradiated PVA/Ag and (c) PVA/PVP/Ag nanocomposites

CONCLUSION

Silver nanoparticles have been prepared by using both of the γ -irradiation and PVP. With these two methods, the reductions of the silver nanoparticles were reduced in the solid phase which provides high restriction against the growth and aggregation of the reduced nanoparticles. In addition, the delay of the reduction process after film drying was found to achieve homogenous dispersion and narrow particle size distribution of nanoparticles within PVA matrix as can be seen from the UV-visible results. The radiation method produces silver nanoparticles with smaller sizes as compared with those formed by polyol method. In addition the polyol method consumes more time to complete the reduction of silver nanoparticles.

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