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Characterization of zein stabilized silver nanoparticles fabricated under gamma irradiation

KEYWORDS: Zein, gamma irradiation, Ag nanoparticle

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ABSTRACT *In this study, we attempted to control the fabrication of Ag nanoparticles using gamma radiation in presence of zein as green stabilizer. The effect of silver ion concentration and zein polymer concentration, on the Ag particle size was studied. The characterization of the silver nanoparticles was done by UV-Visible spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The UV-visible absorption showed the formation of the surface Plasmon resonance peaks corresponding to the Ag nanoparticles in the range of 416-431 nm. A blue shift was observed as the zein concentration increased indicated the formation of smaller particles, while a red shift was observed with increasing the silver ion concentration indicated the formation of larger particles. The XRD confirmed the formation of the silver metal nanoparticles and the TEM imaging reveals that the Ag nanoparticles are spherical in shape, and no aggregates were formed. The as prepared Ag nanodispersions were stable over 9 months at room temperature.*

INTRODUCTION:

The trend of nanomaterial and their applications is acquiring more and more interest day after day. The function nanomaterials are very uniquely and are different from their bulk materials, from isolated atoms or from small clusters [1]. This is due to their high surface to volume ratio and their ability to couple with surface Plasmon of neighboring particles. These nanoparticles represent magic solutions for challenges in different fields such as photonics, electronics, medicine, and pollution treatments.

There are many methods were investigated for preparation of metal nanoparticles; the classical method is the mild chemical reduction for metal salt solutions. Other methods such as the radiolytic and photochemical reduction, the metal ion extrusion from labile organometallic compounds, and metal vapor synthesis techniques were also common. In the radiolytic method, radiation is used to reduce metal salt or complexes in solution by producing solvated radicals in the solution [2]. This method has the advantage of producing metal nuclei homogenously and instantaneously, the narrow particle size distribution is another advantage. In addition, the nanoparticles produced in such methods do not need excessive steps of purification due to the lake of contaminants.

There are two main methods for the stabilization of the metal particles to prevent the metal precipitation or mirror formation: the electrostatic stabilization and the steric stabilization [3]. In electrostatic stabilization, the stabilizer charged particles form double layers that produce Coulombic repulsion between the metal particles. The second method by which colloidal metal particles can be stabilized is by the adsorption of large molecules (polymers or ligands) at the surface of the particles. Synthetic vinyl polymers with polar side groups such as poly(vinylpyrrolidone) (PVP) and poly(vinyl alcohol) (PVA) are examples. Silver nanoparticles in particular are extensively studied as they are finding wide range of applications in catalysis, surface enhanced Raman spectroscopy (SERS) [4-6]. They are known for their antibacterial activity and low toxicity to human cells, which make them a competitive species for the biomedical applications [7-13].

Zein is a potential material for the production of biodegradable plastics due to its thermoplasticity, hydrophobicity and impermeability to gases, and consequently, it considered as one of the best biopolymers that can be used for the preparation of edible and biodegradable films [14-18]. The functionality on the polar part of the zein structure is very attractive for the interaction of zein chains with metal ions.

In this work, gamma radiation was used for the reduction of the silver ions in the presence of the zein solutions as stabilizer. The effect of gamma irradiation on the fabrication and control of Ag nanoparticles were investigated, the properties of produced Ag nanoparticles were characterized in terms of UV analysis, XRD, and TEM.

EXPERIMENTAL:

Material

Silver nitrate, Zein and Ethanol were obtained from (Sigma-Aldrich, Canada Ltd. (Oakville, ON, Canada). all chemicals were analytical grade and used without further purification. All aqueous solutions were made using deionized water.

Preparation of Ag/Zein nanoparticles.

A defined weight of zein (see Table 1) was dissolved in 8 ml of ethanol. Different concentrations of $AgNO_3$ were added to the different zein solutions (see Table 1) under constant stirring. The $AgNO_3$ / zein solutions were irradiated with $^{60}Co\gamma$ -source at different irradiation doses, for the reduction of the silver ions.

Table1: $AgNO_3$ – Zein polymer composition for different prepared samples

Sample No.	Zein/Solvent wt/v (%)	Concentration of $AgNO_3$ (M)
S1	0. 20	0.010
S2	0. 30	0.010
S3	0.50	0.010

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S4	0.50	0.004
S5	0.50	0.014
S6	0.50	0.040

Irradiation

The direct radiation technique was used, in which Zein/silver nitrate solutions were exposed to gamma radiation at constant irradiation doses. The dose rate was determined using a Fricke dosimeter and was found to be 2.86 kGy/h for the self-shielded Indian gamma cell facility installed at the National Center for Radiation Research and Technology, Cairo, Egypt.

UV-Vis spectroscopic analysis

UV-Vis analysis was carried out using a UV2 double beam Unicam, England over the range 200- 800 nm at a high resolution scans.

XRD Analysis.

X-ray diffraction (XRD) experiment of the samples was performed at room temperature by a Philips PW1390 diffractometer (30 kV, 10 mA) with Cu/Ka target irradiation at a scanning rate of 8 degree/min in a 2θ range of 4-90^{O}. The typical diffraction spectrum consists of a plot of reflected intensities versus the detector angle (2θ).

TEM imaging

The morphology of the particles was performed using TEM images model JEM 100CS, Jeol electron microscopy, Japan, working at acceleration voltage of 80 kV.

RESULTS AND DISCUSSION:

Preparation of silver nanoparticles in zien solution

The functional groups on the zien chains have the affinity to interact with metal ions. This advantage was used here to prepare silver nanoparticles in the presence of zein solution as stabilizer. The silver ions when added to the zein solution the functional groups on the zein chains complex with the silver ions. In this concern for all samples silver ions were incubated for 24 h with the zein solutions in order to give enough time for the silver ions to interact with the functional groups on the chains of zein. After that, the gamma irradiation was used for silver ions reduction on the surface of the zien particles. The first observation for all the reduced samples is that the color was turned to brown color and no silver mirror was observed on the glassware, which means that all the formed silver nanoparticles are distributed in the zein solution. Silver nanoparticles are known to exhibit an intense surface Plasmon absorption band in the range of (400- 500 nm) according to the particle size, and the local refractive index near the particle surface [19, 20]. The formation of the silver nanoparticles is confirmed by measuring the surface plasmon absorption spectrum of the silver nanoparticles, using UV-visible spectrometry. The effect of the concentration of the silver ions and zein on the formation of the surface plasmon resonance bands are presented here.

Reduction of silver ions using gamma radiation

Long et al [21] revealed that silver nanoparticles could not be formed at the gamma-ray dose of less than 5 kGy, and no more differences were found for higher doses. A dose of 10 kGy is chosen for the reduction of the silver ions in order to confirm complete reduction. The mechanism of silver ion reduction is explained in scheme 1:

$$H_2O \xrightarrow{Irradiation} e^-_{aq} + H_3O^+ + H^\bullet + H_2 + OH^\bullet + H_2O_2 + \ldots$$

$$Ag^+ + e^-_{aq} \xrightarrow{Reduction} Ag^0$$

$$Ag^0 + Ag^+ \rightarrow Ag_2^+$$

$$Ag^0 + Ag_2^+ \rightarrow Ag_3^+$$

$$(Ag)_n^+ + e^-_{aq} \rightarrow (Ag)_n$$

Scheme 1: mechanism of silver ion reduction by γ radiation.

With increasing irradiation doses above 10 kGy no more differences were found and this may be due to fragmentation that may be occur for higher irradiation doses as shown in scheme 2 :

$$(Ag)_n \xrightarrow{gamma} (Ag)_n^+ + e^-_{aq}$$

$$(Ag)_n^+ + e^-_{aq} \rightarrow (Ag)_n$$

$$(Ag)_n^+ \rightarrow (Ag)_{n-1} + Ag^+$$

Scheme 2: fragmentation of silver nanoparticles under higher irradiation doses.

Effect of zein concentration

The effect of zein concentration on the formation of Ag-zein nanoparticles was studied using different zein concentrations 0.20, 0.30, 0.50% wt/v (S1,S2,S3) with a constant concentration of Ag ions (0.01 M) and irradiated to constant irradiation dose (10 kGy). The UV spectra of the irradiated samples were shown in Figure 1. From the figure, it can be seen that the plasmon resonance peaks were shifted from 431 to 418 nm with increasing the zein concentration. This blue shift indicates the formation of smaller particles [22]. This effect may be due to that the increasing in zein polymer led to a competition between the zein and Ag ions on the solvent radicals formed by irradiation. In addition, the increasing of zien concentration means that more functional groups are available to complex with the silver ions. Consequently, more nuclei can be formed upon reduction resulting in the formation of more particles with smaller size. This conclusion in accordance with the theory of Mie [23], that indicated that nanoparticles with different sizes should demonstrate different optical properties due to the difference in the plasmon resonance bands.

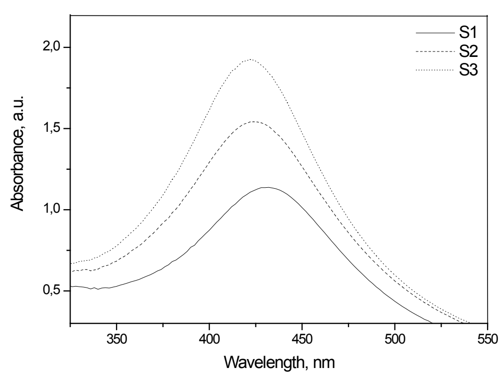

Figure 1. Spectrum of silver surface plasmon band obtained from constant Ag concentration (0.01 M) and different zein concentrations: S1 (0.2), S2 (0.3), S3 (0.5) (wt\v).

Effect of $AgNO_3$ concentration

Silver ions with different concentrations were reduced in zien solutions using 10 kGy γ irradiation. The samples were prepared with a constant zein concentration (0.5% wt/v) and varied silver nitrate concentrations 0.004, 0.014, 0.04 M (S4-S6). The spectrophotometric measurements of the silver nanoparticles surface plasmon for samples show increment of the intensity of the surface palsmon with increasing the concentration of the silver ions (Figure 2). A red shift is also observed for the samples prepared with higher silver ion concentrations from 416 to 426 nm. This observation suggests the formation of larger silver nanoparticles. In general all the plasmon spectra observed shows no splitting, which means that uniform shape was formed and there are no elongated

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silver nanoparticles exists [24, 25]. Moreover, the symmetry in the spectra suggests homogeneous spherical silver nanoparticles [25], as will be confirmed by the TEM results later on.

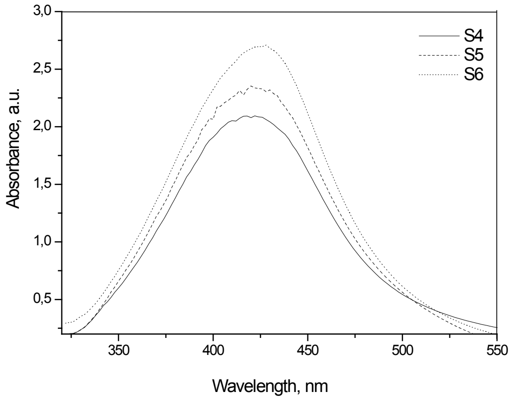

Figure 2. Spectrum of silver surface plasmon band obtained from constant zein concentration (0.5 wt/v %) and different $AgNO_3$ concentrations: S4 (0.004), S5 (0.014) and S6 (0.040) M.

XRD analysis

Effect of Zein concentration on XRD

XRD is an effective tool to characterize the crystal type, size and d-spacing. Figure 3 Showed the XRD spectra for gamma irradiated Zein/$AgNO_3$ solution S1 and irradiated to 10 kGy. From Figure 3 it can be seen that the Ag peaks at (2θ) equal to, 38.1, 46.3, 67.47, and 76. 9, which attributed to (111), (200), (220) and (311) crystalline planes of phase centered cubic crystal of metallic Ag respectively. This confirms the formation of the silver nanoparticles as shown in Figure 3.

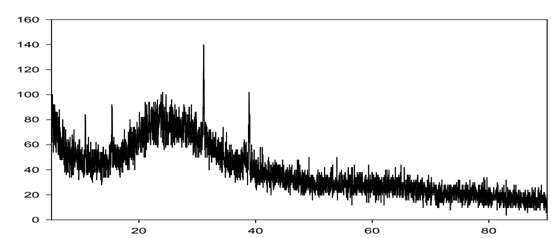

Figure 3. XRD spectra for Ag particles prepared by 0.20 % wt/v zein/ 0.01 M $AgNO_3$ solution (S1).

The average crystallite size of Ag calculated from Scherrer formula as following.

$D=0.94\lambda W \cos\theta$

Where W represent the peak full width at half maximum intensity (FWHM) of the peak (111),□ λ is the wavelength for CuKα(□λ = 0.15418 nm) and D is the crystalline size in nm. The calculated crystallite size (d), lattice constant (a), and unit cell volume (V) values are listed in Table 2.

Table 2. XRD parameters for Ag particles prepared by gamma irradiation to zein/$AgNO_3$ solution at different zein concentration

Sample code	Dose (kGy)	d (nm)	a (nm)	V (nm^3)
S1	10	1.1241	4.0088	6.44233
S2	10	1.6908	4.0122	6.45893
S3	10	0. 3290	4.0836	6.80958
S4	10	1.7873	4.0670	6.72697
S6	10	5.5517	4.0587	6.68572

lattice constant (a), unit cell volume (V) and crystalline size (d)

From Table 2 it can be seen that increasing in the zein concentration led to a decrease in the a, d and V values of Ag crystallite, which is in good agreement with UV-visible results

The centered cubic crystal (FCC) of silver metal has a unit cell edge **'a' = 4.07 A°** and this value is calculated theoretically

$$a = 4/\sqrt{2} \times r$$

For silver r =144 pm, in our experiment the lattice constant 'a' is calculated from the most intense peak (111) of the XRD pattern and was found to be 3.8035 - 4.0836 A° (the values are listed in Table 2). Both theoretical & experimental lattice constant 'a' are in close values. The values in the literature report (a = 4.086 A, JCPDS file no.04-0783).

TEM analysis

Figure 5 a-d is showing the TEM images of different silver stabilized zein solutions. The images indicate that all the formed silver nanoparticles have spherical shape and no other shapes were observed. This result is agreeing well with the results of the UV-visible spectroscopy. In addition there are no large aggregates were formed which mean that the stabilization of zein chains for the formed silver nanoparticles was successful. Figure 5 a, b shows images of S1 and S2 prepared with the same concentration of silver ions (0.01 M) and different zein concentrations 0.2 % and 0.3 % respectively and irradiated with the same radiation dose (10 kGy). It is noticeable that the silver nanoparticles formed in S1 (lower concentration of zein) are larger than those formed in S2 with higher concentration of zein (see Figure 5 a, b). This is in good agreement with the UV-visible absorption and XRD results.

On the other hand, the samples prepared with the same zein concentration (0.5 % wt/v) and different silver nitrate concentrations; S5 (0.014 M) and S6 (0.040 M) and exposed to 10 kGy irradiation dose, are shown in Figure 5c, d. The density of the formed silver nanoparticles in S6 is pronouncedly higher as shown in the figure. In addition larger Ag nanoparticles were formed as the concentration of Ag ions was increased (see Figure 5c, d). In general the results indicate that as the amount of the functional groups of zein increases in relation to the concentration of the silver ions, more nuclei are formed upon reduction. This results in the formation of smaller silver nanoparticles.

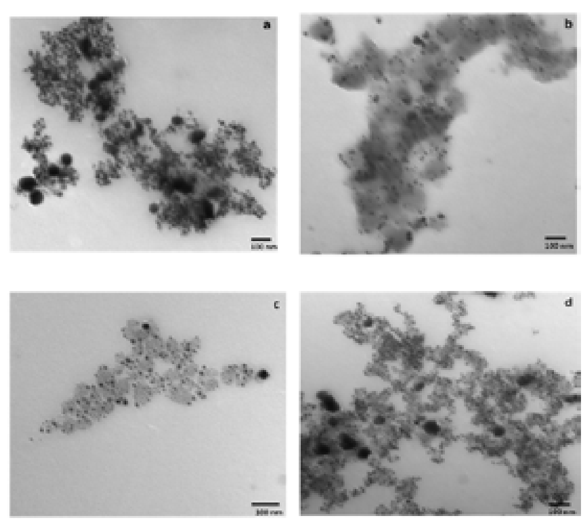

Figure 5. TEM images of Ag nanoparticles prepared from zein/$AgNO_3$ at different compositions: a (S1), b (S2), c(S5) and d(S6).

Conclusions:

In conclusion, zien solutions were successfully used as green stabilizer for silver nanoparticles. The gamma radiation can be used for the reduction of the silver ions forming nanosized and spherical shape particles in. It was also confirmed that the size of the Ag particles and consequently their plasmonic properties can be controlled over tuning the concentration of the components.

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