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Starch-Capped Silver Selenide Nanoparticles: Effect of Capping Agent Concentration and Extraction Time on Size

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Starch as capping molecule has been used increasingly as part of the green chemistry concept of synthesis and in this work is used to stabilize silver selenide nanoparticles. The influence of extraction time and capping agent concentration were studied to investigate their effect on the size of the synthesized nanoparticles. Silver selenide has good potential in antibacterial activity but that depends on the shape and sizes of the nanoparticles. The FT-IR and UV-visible spectroscopy, TGA, TEM and XRD techniques have been used to characterize the prepared silver selenide nanoparticles. The prepared nanoparticles gave size distribution of the diameters of 1-9 nm. The size of nanoparticles was found to decrease with an increase in extraction time 0 to 20 h. With an increase in the concentration of starch, 0.025 to 0.1 w/v, nanoparticles size decreased and then increased at higher capping concentration, which was due to ripening effect.

Keywords: Starch, Silver selenide, Nanoparticles, Extraction time, Capping agent.

INTRODUCTION

Nanomaterials may provide solutions to technological and environmental challenges in the areas of solar energy conversion, catalysis, medicine and water treatment [1]. Silver selenide (Ag_2Se) is a phase change material that consists of two crystalline phases. It possesses a stable β-Ag_2Se crystal phase with orthorhombic structure below 133 °C. β-Ag_2Se is a narrow band gap semiconductor. It has the energy band gap between 0.07 and 0.15 eV and has low thermal conductivity and high electrical conductivity. Above 133 °C, Ag_2Se possesses a stable, super-ionic α-Ag_2Se crystal phase with cubic structure at high temperatures [2,3]. Researchers have paid much attention to metal selenide nanoparticles due to their interesting properties and they have been used as optical filters, optical recording materials and biomedical labeling [4,5]. A number of methods (physical and chemical) have been reported for the synthesis of Ag and Ag_2Se nanoparticles and includes the use of organic and inorganic reducing reagents, electrochemical techniques, physico-chemical reduction and radiolysis. In order to reduce aggregation and improve stability of nanoparticles, it is important to modify their surface. Biopolymers have been reported to be the good materials to control reaction environments for controlled growth of metallic as well as semiconductor nanoparticles [6]. Among the biopolymers used, starch takes preeminence. This is because it is inexpensive, hydrophilic, non-toxic, biocompatible, biodegradable, renewable and safe. It is readily available from agriculture as the major component of carbohydrates. Its biodegradable nature may also be exploited and used to aid in the reduction of cytotoxicity problems associated with the use of quantum dots and thus extend their application to food and pharmaceutical products [4]. This work report the green synthesis of starch capped Ag_2Se nanoparticles and the effect of starch capping agent concentration and extraction time on the size, optical and morphological properties of Ag_2Se nanoparticles. The nanoparticles have been prepared at room temperature with water as a solvent and starch as a capping molecule. This green synthesis method has been adapted as a result of the increasing need to develop environmentally friendly processes, where no toxic chemicals will be used in the synthesis procedures [7]. Starch has been used as it is a good polymer to cap nano-sized materials because of OH^- polar groups in the structures, which act as coordination sites for ion aggregation between particles [4,8]. It is also environmental friendly and biocompatible.

EXPERIMENTAL

Selenium powder (99.5, 100 mesh) sodium borohydride (98.5 %), silver nitrate (99 %), ammonium hydroxide (99.9 %), soluble starch (99.9 %) were purchased from Merk (Germany). All chemicals were used as purchased, without any further purification.

Synthesis of starch capped Ag_2Se nanoparticles: To prepare the selenium precursor solution, selenium powder

(0.32 mmol) was added to deionized water (20 mL) in a three-necked flask at room temperature. Sodium borohydride (0.81 mmol) was then added to this reaction mixture and the flask was immediately purged with nitrogen gas to create an inert atmosphere. The reaction mixture was then stirred for 2 h at room temperature. Starch capped silver selenide nanoparticles were prepared by adding a solution of silver nitrate (1 mL, 0.32 mmol) to a soluble starch solution (20 mL, 0.025-0.1 w/v) in a one-necked round-bottom flask with constant stirring at room temperature. The pH of the solution was adjusted to 11 using ammonium hydroxide (0.1 M). This was followed by addition of the colourless selenide ion solution (1 mL). The reaction mixture was further stirred for 0-20 h at room temperature to complete the reaction. The resultant solution was then centrifuged and extracted with acetone to obtain a grey-black precipitate of Ag_2Se nanoparticles. The precipitate was washed several times and dried at room temperature.

Effect of extraction time: To monitor the progress of the reaction, UV-visible spectroscopy was used. The effect of extraction time was investigated over a period of 20 h at 5 h intervals. 10 mL aliquots of the sample was extracted every 5 h and analyzed with UV-visible spectroscopy. The TEM instrument was used to view the size and shape of the nanoparticles formed during the course of the reaction process.

Effect of capping agent concentration: The capping agent is crucial in the control of particles size and affects agglomeration and morphology of nanoparticles. To investigate the effect of the capping agent, different concentrations of the capping agent (starch) (0.025, 0.05 and 0.1 w/v) were used. The resultant nanoparticles were analyzed using FT-IR, UV-visible spectroscopy, TEM, XRD techniques The conditions (extraction time and capping agent concentration) investigated are shown in Table-1.

TABLE-1
VARIATION OF REACTION CONDITIONS

Sample	Capping agent concentration (%)	Extraction time (h)
A	0.050	0
B	0.050	5
C	0.050	10
D	0.050	15
E	0.050	20
F	0.025	20
G	0.100	20

Characterization: UV-visible spectral studies were performed at 200-1100 nm wavelength range and at room temperature, using Perkin Elmer Lamda 25 UV-visible spectrophotometer. The samples were placed in quartz cuvettes cell of 1 cm path length for measurements. Perkin Elmer spectrum 400 FT-IR-NIR spectrometer equipped with a universal ATR sampling accessory was used to perform Fourier transform infrared (FT-IR) analyses. A JEOL JEM-2100 transmission electron microscope operating at 200 kV was used to study the microstructure of the nanoparticles. The TEM was coupled with an energy dispersive X-ray (EDX) detector which was also used to determine the elemental composition of the synthesized nanoparticles. The samples were prepared by putting an aliquot solution of the water soluble nanocrystalline material onto an amorphous carbon substrate supported on a copper grid and then the solvent was allowed to evaporate at room temperature prior the analysis.

The surface morphology of the nanocrystals was visualized using a quanta VEGA 3 TESCAN scanning electron microscope (SEM). The samples were placed on a carbon tape and analysed without gold coating for the analysis. The X-ray diffraction patterns were recorded by a Bruker D2 diffractometer at 40 kV and 50 mA. A secondary graphite monochromated CoK_α radiation ($\lambda = 1.7902$ Å) was used and the measurements were taken at high angle 2θ in a range of 5-90° with a scan speed of $0.01°\ 2\theta\ s^{-1}$. A Perkin Elmer Thermogravimetric Analyzer (TGA 4000) was used for thermal analysis. The samples were heated under nitrogen at a heating temperature of 25 to 900 °C and a heating rate of 5 °/min.

RESULTS AND DISCUSSION

Starch is a semicrystalline polymer composed of two polysaccharides, *i.e.*, amylose and amylopectin. Amylose is a linear chain which consists of glucose molecules which are interconnected by α-1,4-glycosidic linkages. Amylopectin is a large, highly branched macromolecule which consists of linkages of α-1,4- and α-1,6-glycosidic linkages. The α-1,4 linkages function as the backbone while the α-1,6-glycosidic bridges function as the branching points. The presence of the large number of hydroxyl groups in the glucose monomers can help in facilitating the complexation of metallic ions to the starch matrix, while nano-supramolecular structures formed by intermolecular and intramolecular hydrogen bonding can act as templates for the growth of nanoparticles. These properties thus make starch a good candidate for nanoparticles' passivation. The utilization of starch as a passivating agent is also advantageous because it can assist in achieving green synthesis of nanoparticles. These advantages include among others: (i) starch is highly dispersible in water thus can help to eliminate the use of organic solvents, (ii) makes the separation of particles feasible because the binding interaction between starch and nanoparticles is relatively weaker compared to the interaction between the nanoparticles and typical thiol-based protecting groups and (iii) starch-protected nanoparticles are readily integrated into biological systems and thus makes them relevant for pharmaceutical and biomedical applications [4,9]. The overall chemical reaction involved in the synthesis of starch-capped nanoparticles is represented by the following equations:

$$4NaBH_4 + 2Se + 7H_2O \rightarrow 2NaHSe + Na_2B_4O_7 + 14H_2 \quad (1)$$

$$AgNO_3 + \text{Startch} \rightarrow \text{Ag-starch complex} \quad (2)$$

$$\text{Ag-starch complex} + HSe^- + OH^- \rightarrow \text{Starch-}Ag_2Se + H_2O \quad (3)$$

$$HSe^- + OH^- \longrightarrow Se^{2-} + H_2O \quad (4)$$

Eqn. 1 represents the reduction of selenium powder in aqueous medium at room temperature under an inert atmosphere. This results in the formation of highly active hydrogen selenide ions. Eqn. 2 shows the reaction of the metal nitrate with starch generating starch-metal ion complex. It is important to note that in an aqueous medium, starch adopts a right-handed helical conformation. The helical conformation exposes the abundant hydroxyl groups and thus assist in the complexation of metal ions to the molecular matrix. The starch-metal ion complex then reacts with the active HSe^- ions under an alkaline medium resulting in the production of starch capped metal selenide nanoparticles (eqn. 3). The addition of hydrogen selenide ion solution to the starch-metal ion solution gradually releases selenide ions (Se^{2-}) upon hydrolytic decomposition in alkaline media as represented in eqn. 4. The released selenide ions then react with metal ion to form seed particles (nucleation). The OH groups of starch thus act as coordination sites for the release of the metal ions and thus control the chemical reaction rate of the combination of M^+ and Se^{2-} to produce MSe nanoparticles. These hydroxyl groups also act as passivating centres and thus help in the stabilization and solubility of the as-synthesized nanoparticles in water. The free aldehyde group on the other end of the starch polymer could also act as the conjugation site for further functionalization which makes it easier for its biological applications [4,10].

Optical analysis of starch capped Ag_2Se nanoparticles

Effect of reaction time: The absorption spectra of starch capped silver selenide nanoparticles at different extraction times (0, 5, 10, 15 and 20 h), synthesized with 0.05 w/v of starch using 0.32 mmol monomer (Ag, Se) concentrations are shown in Fig. 1. By varying the reaction time, the growth of the synthesized nanoparticles was monitored. The absorption spectra were characterized by tailing band-edges with no distinctive excitonic features at lower reaction times (0-10 h) which indicates the presence of large nanoparticles. As the reaction proceeded, a distinctive excitonic shoulder appeared at 460 nm. The absorption shoulders were all blue-shifted in relation to the bulk band gap. The absorption band edges of the nanoparticles at 15 and 20 h were observed to be similar. The presence of bands in the UV region of the spectrum are attributed to n-π* excited transition of the starch capped Ag_2Se nanocomposite [4]. The intensity of the absorbance peak increased at 15 h and further increased as the reaction time increased, which indicated the continuous reduction of the silver selenide ions. The increase in absorbance with the increase in extraction time also indicates that the concentration of Ag_2Se nanoparticles is also increasing. This occurrence indicated that the size of particles decreased as the reaction time increases because the absorbance peak showed a blue shift. The similar pattern has also been observed by Darroudi *et al.* [11]. Time 20 h was then chosen as the best extraction time for the production of starch capped silver selenide nanoparticles.

Effect of capping agent concentration: The absorption spectra of starch capped silver selenide nanoparticles with different capping agent concentration (0.025, 0.05 and 0.1 w/v), synthesized using 0.32 mmol monomer concentrations as shown in Fig. 2. The nanoparticles synthesized with 0.025 and 0.1 w/v of starch showed an absorption peak at 470 nm (2.63 eV), while the 0.05 w/v capped nanoparticles exhibited an absorption peak at 460 nm (2.69 eV). This observation meant that at 0.05 w/v starch concentration smaller nanoparticles were formed while 0.025 and 0.1 w/v starch concentration bigger nanoparticles were formed. This was also confirmed by the TEM results.

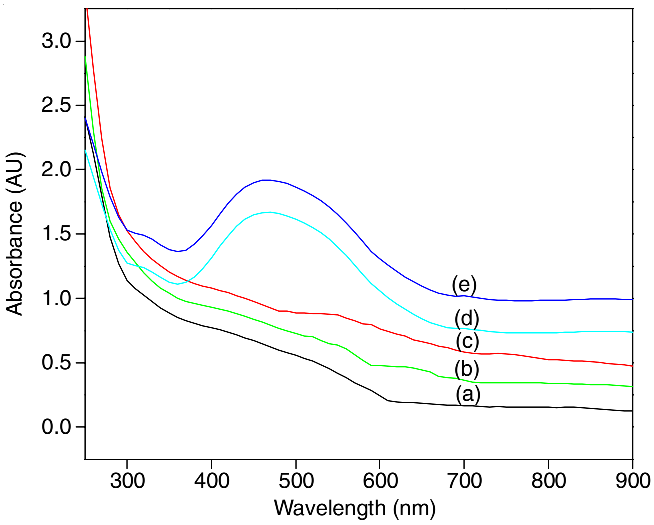

Fig. 1. UV-visible spectra for starch capped Ag_2Se (1:1), with 0.05 w/v starch at 0 h (a), 5 h (b), 10 h (c), 15 h (d) and 20 h (e)

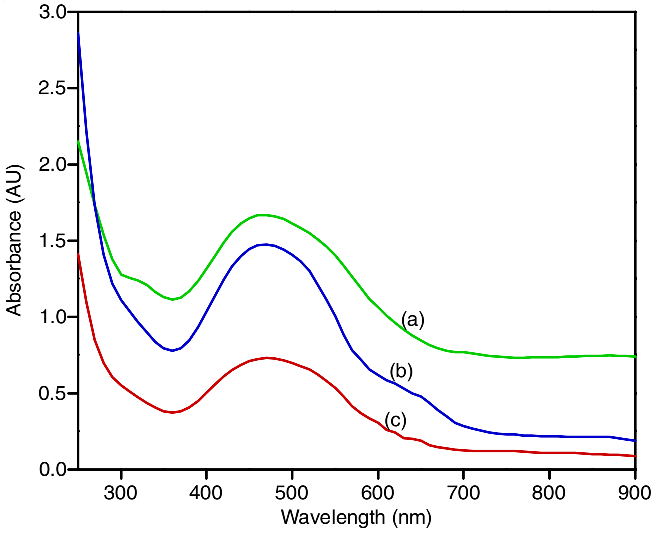

Fig. 2. UV-visible spectra for starch capped Ag_2Se (1:1) nanoparticles with 0.025 w/v (a), 0.05 w/v (b) and 0.1 w/v (c) of starch

FT-IR spectral analysis: Starch-capped Ag_2Se nanoparticles investigated by using FT-IR in order to study the present functional groups in comparison to pure starch. The FT-IR spectrum (Fig. 3) shows the spectrum of the functional groups present in starch and starch-capped Ag_2Se nanoparticles. A strong band at 3295 cm^{-1} is attributed to the O-H stretching of starch. The band observed at 2930 cm^{-1} is attributed to asymmetric stretching of C-H. The band at 1643 cm^{-1} is attributed to water adsorbed in the amorphous region of starch. The band observed at 1415 cm^{-1} is due to both the CH_2 bending and the C-O-O stretch. The angular deformation of C-H was observed at 1337 cm^{-1}, while band at 1244 cm^{-1} is assigned to a CH_2OH (side chain) related mode. The bands at 1149 cm^{-1} and 1077 cm^{-1} are attributed to the C-O, C-C stretching and C-O-H bending of starch, respectively. The noticeable band at 996 cm^{-1} is attributed to the skeletal mode vibration of α-1,4-glycosidic linkage (C-O-C)while the band at 761 cm^{-1} is attributed to C-C stretching [4,12-14]. The presence of starch characteristic bands in the synthesized nanoparticles confirmed the capping of the nanoparticles with starch. The wavenumber shift of the

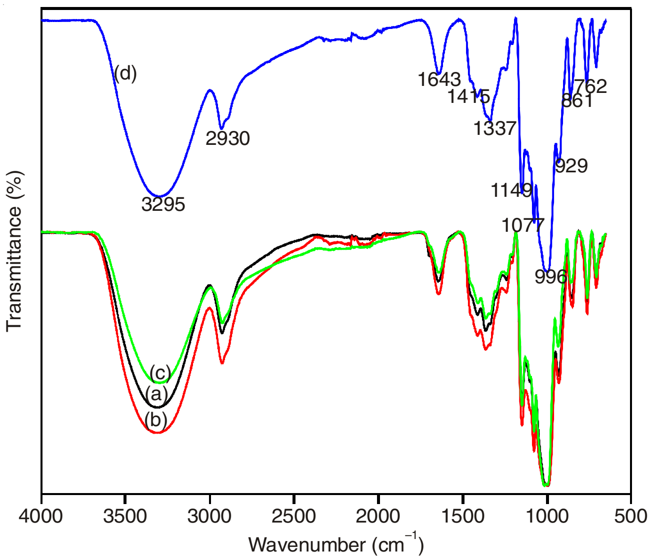

Fig. 3. FT-IR spectra of starch capped Ag_2Se nanoparticles with 0.025 w/v (a), 0.05 w/v (b), 0.1 w/v (c) and pure starch (d)

OH group and CH_2OH side chain on the starch capped nanoparticles is a result of the binding of starch with the metal.

TGA analysis: Fig. 4 shows TGA plot of starch capped silver selenide nanoparticles. The weight loss observed below 100 °C is due to the desorption of water from the nanoparticles, while the loss at 310 °C is the onset of starch decomposition and the residue of Ag_2Se nanoparticles remained. Since there is no endorthermic peak observed in the derivative curve above 310 °C, it indicates that there is no further chemical or physical change occuring to the nanoparticles. The residue of Ag_2Se continues to show decomposition due to relative nanoparticles volatility as compraed to the bulk Ag_2Se.

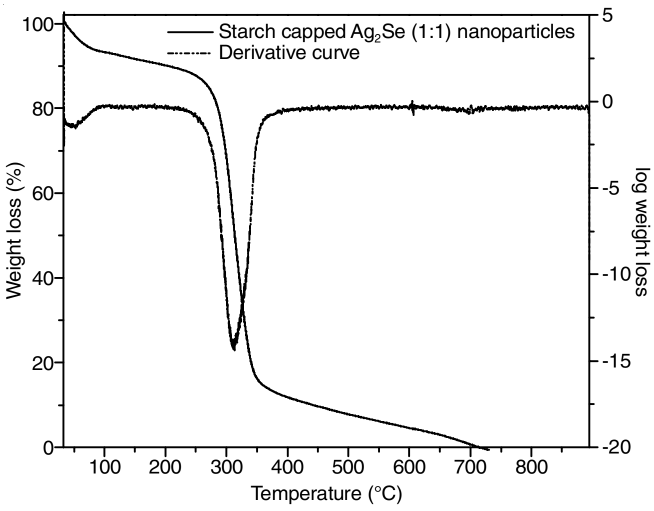

Fig. 4. TGA and derivative thermograms of starch capped Ag_2Se nanoparticles with 0.05 w/v of starch

TEM analysis

Effect of extraction time: The TEM images revealed that the increasing of the reaction time resulted in the synthesis of smaller sized nanoparticles (Fig. 5). The mean particle sizes were calculated to be 9.72 nm and 1.92 nm for 15 and 20 h, respectively. This decrease in particle size as the reaction time increases could be attributed to digestive ripening of the nanoparticles. The decrease in nanoparticle size with increase in extraction time as observed in this work is consisted with work reported by Oluwafemi and Revaprasadu [4]. As the reaction time increases, the amount of hydroxyl ions increases thus leading to an increase in the particle size. When its concentration exceeds the Ag^+ ions, the role is taken over by Ag^+ which then becomes the limiting reactant. At this point the amount of available free Ag^+ is shared by the selenide ions in the solution and the free hydroxyl ions for the formation of the nanoparticles and Ag^+ hydroxyl complex respectively. This then leads to a decrease in the particle size [4]. The TEM results also indicated that with an increase in time the nanoparticles retain a narrower particle size distribution.

Effect of capping agent concentration: The capping agent also plays an important role in the morphology and properties of nanoparticles. The results obtained when varying the concentration of the capping agent from 0.025 to 0.1 w/v are shown in Fig. 6. The TEM studies revealed that the 0.025 w/v capping agent resulted in quite irregular and severely aggregated nanoparticles. This indicated that the amount of the capping agent used was insufficient therefore could not form a complete protective layer thus the particles aggregated easily. For 0.05 w/v starch concentrations well dispersed nanoparticles were observed. A decrease in nanoparticle size with an increase in capping agent concentration was observed from 0.025 to 0.05 w/v starch. This could have been strongly influenced by the number of nuclei formed at a given time, which favours a fast autocatalytic growth thus giving rise to a large number of small particles [15]. The results obtained are in agreement with the results reported by other researchers on their investigation of the effect of capping agent concentration on nanoparticle size [16-18]. The starch concentration of 0.1 w/v also gave well dispersed nanoparticles with larger particles as compared to lower percentage (0.05 w/v) This could be due to diffusion of smaller particles through the solution and add to the surface of other nanoparticles thus form larger nanoparticles regarded as growth by ripening. Growth by ripening can take place during the whole process because a slow chemical reaction favours continuous nuclei formation thus always keeping a certain number of nuclei present in the system. This therefore means that a slow reaction rate, nucleation and growth occurred simultaneously leading to the formation of larger nanoparticle sizes [15]. The calculated particle sizes from the TEM images were found to be 8.78 nm (0.025 w/v starch), 1.92 nm (0.05 w/v starch) and 9.96 nm (0.1 w/v starch). EDX analysis was done to confirm the presence of silver and selenium in a ratio of 1 to 2 corresponding to the formula of silver selenide, Ag_2Se. Other elements were observed such as copper obtained from the sample preparation.

XRD analysis: Fig. 7 shows the XRD parttens of the prepared starch capped Ag_2Se nanoparticles. The diffraction peaks of the products can be indexed to orthorhombic phase Ag_2Se (JCPDS card 03-065-2625).

Factors such as concentration, temperature, capping agent as well as the reaction time are important parameters that have an effect on the size and the morphology of the nanoparticles. The concentration of capping agent controls the particles size as well as protects the particles from coagulation [19]. As the reaction time increases, the amount of hydroxyl ions increases

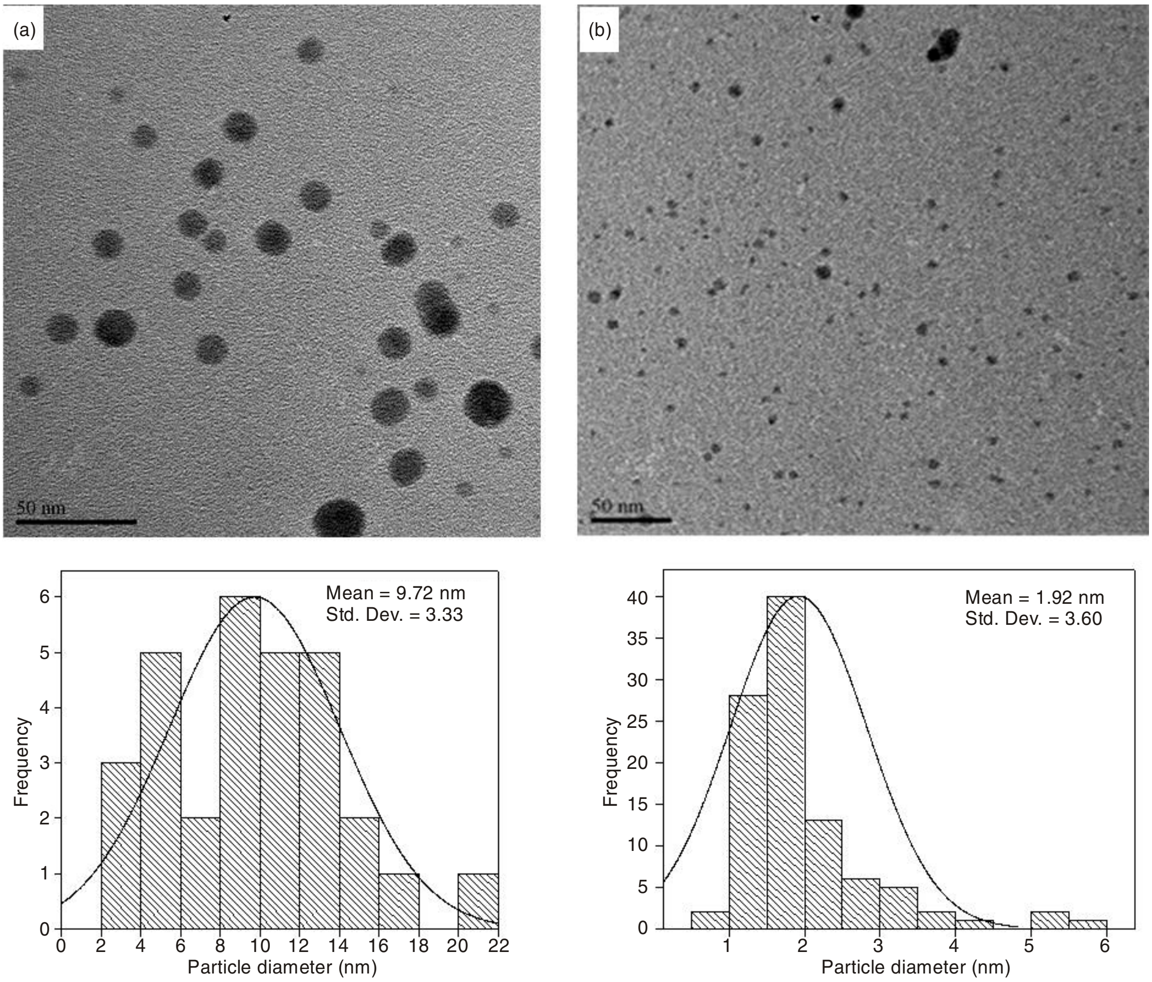

Fig. 5. TEM images and histograms for starch capped Ag_2Se nanoparticles prepared at 15 h (a) and 20 h (b)

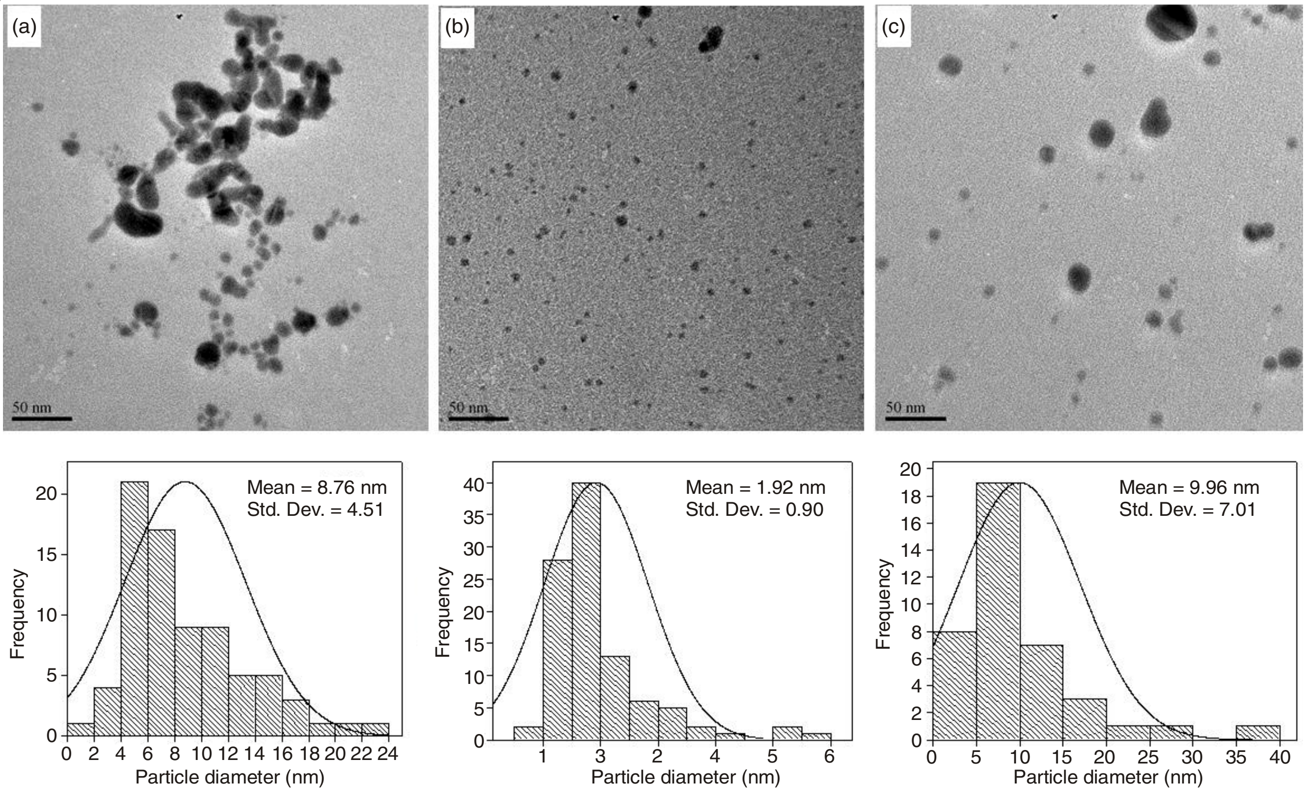

Fig. 6. TEM images of starch capped Ag_2Se nanoparticles with 0.025 w/v (a), 0.05 w/v (b) and 0.1 w/v (c) starch

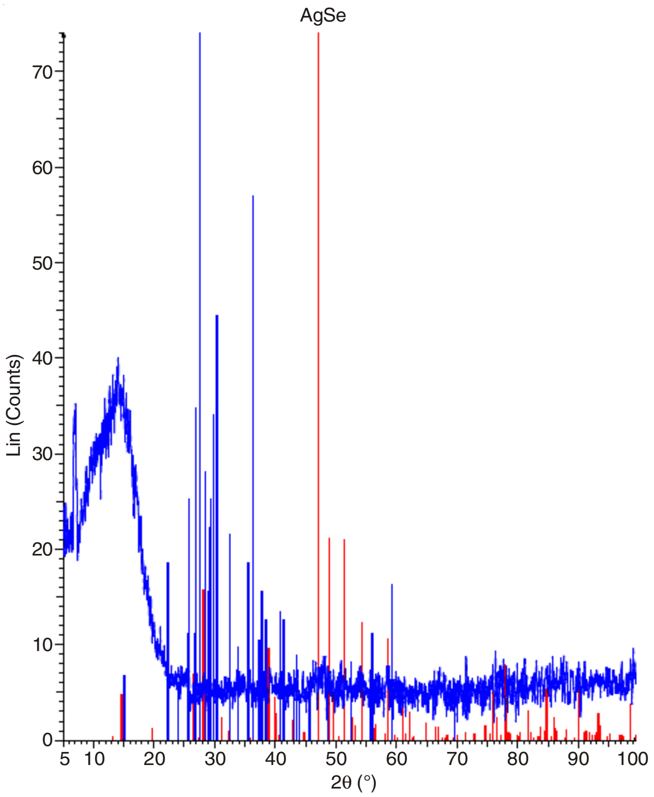

Fig. 7. XRD patterns of starch capped Ag_2Se nanoparticles

thus leading to an increase in the particle size. As its concentration exceeds that of Ag^+ ions, Ag^+ becomes the limiting reactant. The amount of available free Ag^+ is then shared by the selenide ions in the solution and the free hydroxyl ions for the formation of the nanoparticles. This then leads to a decrease in the particle size. For these reasons the effect of capping agent concentration and extraction time on the size of nanoparticles were investigated.

Conclusion

The synthesis of starch capped silver selenide nanoparticles was studied under different reaction conditions. The effect of extraction time and capping agent concentratin on the synthesis of silver selenide nanoparticles were investigated. These quantities were investigated in order to achieve optimal and suitable conditions for the production of silver selenide nanoparticles. The present investigation indicated that an increase in capping agent concentration results in a decrease in nanoparticle size and then increased at higher capping concentration. The increase in extraction time showed a decrease in nanoparticle size. Thermogravimetric analysis showed that the prepared nanoparticles are stable up to 310 °C and then decompose. TEM results showed that the nanoparticles obtained are spherical in shape and they are not agglomerated. XRD results indicated that Ag_2Se nanoparticles have been prepared successfully in an orthorhombic phase.

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