DE GRUYTER Green Process Synth 2017; 6: 183–188

Nokwethemba Precious Sibiya and Makwena Justice Moloto*

Shape control of silver selenide nanoparticles using green capping molecules

DOI 10.1515/gps-2016-0057
Received March 30, 2016; accepted August 16, 2016; previously published online December 19, 2016

Abstract: Employing a capping agent during the synthesis of nanoparticles has been reported to play a role in controlling size and shape of the nanoparticles. Due to this reason, this study reports the synthesis of silver selenide nanoparticles using different environmentally friendly capping agents (green tea, glucose, ascorbic acid and chitosan) in order to investigate their effect on the size and shape of the nanoparticles. Transmission electron microscopy (TEM) results showed that the nanoparticles have different shapes (rods, spheres and cubes) with an average size of 8–96 nm depending on the capping agent used. Fourier transformer infrared (FTIR) spectroscopy confirmed that the capping of nanoparticles was successful, while X-ray diffraction (XRD) showed that the nanoparticles have an orthorhombic phase.

Keywords: capping agents; nanoparticles; orthorhombic phase; silver selenide.

1 Introduction

Silver selenide (Ag_2Se) is a semiconductor which has gained attention due to its importance in many applications such as thermoelectric cooling materials, high electrical conductivity, photo chargeable secondary batteries, ion selective electrodes, electrochemical storage cells, electrochemical memory devices, infrared sensors, solar sensors, optical filters and photolithography, superionic materials, laser materials and biological labels [1, 2]. The size and shape-dependent variation in properties of matter is one of the attracting aspects of science at the nanoscale range. As a result of this, researchers have dedicated much effort in order to control the parameters involved in size and morphological variations to develop a well-defined structure with specific physical and chemical properties. Capping agents play a crucial role in controlling morphology of the nanostructure due to their soft-template effect, their ability to modify the chemical kinetics and the ability to be maneuverable [3]. It is crucial to effectively cap the metal nanoparticles as the surface activity of nanoparticles makes them agglomerate and form a larger size group with a number of weak interfaces. By adding the capping agent, growth of reunion of particles can be prevented, thus improving the dispersion of the nanoparticles. In the chemical capping method, the concentration of the capping agent controls the particles size and also prevents the particles from aggregation [2, 4]. Also capping agents have been reported to have an effect on the morphology of nanoparticles. Ag and Ag_2S nanoparticles have been synthesized using various surfactants and different morphologies were obtained. Cubic structures of Ag nanoparticles were obtained using sodium dodecyl sulfate, while spherical structures were obtained with propylene glycol. Nanorods and nanospheres of Ag_2S were obtained using ethylenediamine, while nanospheres were obtained with propylene glycol [5]. Flower-like CdS nanorods have been synthesized using propylene glycol and thioglycolic acid by Salavati-Niasari et al. [6].

In order to modify the nanoparticles surface, different capping molecules (chitosan, glucose, green tea and ascorbic acid) have been used as a surface capping agent for stabilizing the nanoparticles and to control the particle size. Chitosan is a naturally occurring polymer which is an antibacterial and bioactive polymer with momentous amounts of amine and hydroxyl groups [7, 8]. Glucose is a monosaccharide found in plants, with five hydroxyl groups that are arranged in a specific way along its six carbon backbone [9]. Green tea is a product made from the *Camellia sinensis* plant. It contains polyphenols which forms complexes with metal ions in solution and reduces them to the corresponding metals. The polyphenols act as both the reducing as well as the capping agent and thus affect the growth on the nanoparticles [10]. Ascorbic acid is a naturally occurring organic compound which has antioxidant properties [11]. The use of natural compounds is important in the synthesis process of nanoparticles because they are biocompatible, ecofriendly and they reduce the environmental pollution by replacing the toxic compounds that are commonly used [12]. Natural compounds have been used as reducing as well as capping

---

***Corresponding author: Makwena Justice Moloto,** Vaal University of Technology, Department of Chemistry, Private Bag X021, Vanderbijlpark, 1900, South Africa, e-mail: makwenam@vut.ac.za
Nokwethemba Precious Sibiya: University of KwaZulu Natal, Department of Chemistry, Private Bag X01, Scottsville, 3209, South Africa

agents for the synthesis of nanoparticles. Ansari et al. [12] synthesized $NiTiO_3/NiFe_2O_4$ nanocomposites using onion extract as a reducing and capping agent and obtained a star-like morphology. Oluwafemi and Revaprasadu [13] synthesized the starch capped CdSe and obtained nanorods, nanowires and spheres depending on the precursor concentrations used. Green tea capped silver and palladium nanoparticles were prepared by Nadagouda et al. [10] and spherical nanoparticles were obtained. This work therefore reports on the simple and cheap method for synthesis of silver selenide nanoparticles at room temperature using glucose, ascorbic acid, chitosan and green tea as reducing and capping agents. These compounds were used because they are environmentally friendly, bio-compatible and biodegradable. Also, water, which is a non-toxic, cheap, available, interminable solvent, was used at room temperature. The capping agent effect was investigated because they control the size, shape and agglomeration of nanoparticles. To the best of our knowledge, this paper reports for the first time the capping of silver selenide using these green capping agents.

2 Materials and methods

2.1 Chemicals

Selenium powder (99.5%, 100 mesh), sodium borohydride ($NaBH_4$) (98.5%), silver nitrate ($AgNO_3$) (99%), ammonium hydroxide (NH_4OH) (99.9%) and D-glucose reagent grade were purchased from Merck (Darmstadt, Germany). Acetone (99.8%), ascorbic acid and chitosan reagent grades were purchased from Sigma Aldrich (Aston Manor, Johannesburg, South Africa). All chemicals were used as purchased, without any further purification.

2.2 Synthesis of Ag_2Se nanoparticles: effect of capping agents

The methodology used for the synthesis of Ag_2Se nanoparticles in the aqueous phase was adopted from Oluwafemi and Revaprasadu [2] with some modification. To prepare the selenium precursor solution, selenium powder (0.1 M) was added to deionized water (20 ml) in a three-necked flask at room temperature. Sodium borohydride was then added to this reaction mixture and the flask was immediately purged with nitrogen gas. The reaction mixture was then stirred for 2 h at room temperature. A solution of 0.1 M silver nitrate was added to 1.0% of each capping agent (glucose, ascorbic acid, chitosan, green tea) 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. This was followed by addition of the colorless selenide ion solution. The reaction mixture was further stirred for 20 h at room temperature to complete the reaction. The resultant solution was then centrifuged and extracted with methanol to obtain a precipitate of Ag_2Se nanoparticles. The precipitate was washed several times and dried at room temperature. The effect of the capping agent was investigated using different capping agents green tea, glucose, ascorbic acid and chitosan.

2.3 Characterizations

A UV-Vis spectrophotometer (Perkin Elmer Lamda 25) was used to carry out optical analysis at room temperature at 200–1100 nm wavelength range. Fourier transform infrared (FTIR) spectral studies were carried out using a Perkin Elmer spectrum 400 FTIR-NIR spectrometer equipped with a universal ATR sampling accessory. The nanoparticle structure was studied using a JEOL JEM-2100 transmission electron microscope operating at 200 kV. The transmission electron microscopy (TEM) was coupled with an energy dispersive X-ray detector which was used to determine the elemental composition of the synthesized nanoparticles. The samples were prepared by placing 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 dry at room temperature. The X-ray diffraction (XRD) patterns were recorded using a Bruker D2 diffractometer at 40 kV and 50 mA and a secondary graphite monochromatic Co Kα radiation ($l=1.7902$ A°). 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 PerkinElmer thermogravimetric analyzer (TGA 4000) was used for thermal analysis. The samples were heated under nitrogen and the heating range was between 25°C and 900°C at a heating rate of 5°/min.

3 Results and discussion

3.1 Optical and structural analysis

The effect of capping agent (green tea, glucose, ascorbic acid and chitosan) on the optical properties of silver selenide nanoparticles (Ag_2Se NPs) is shown in Figure 1. Ag_2Se-NPs showed a peak at 361 nm for green tea, for glucose at 360 nm, for ascorbic acid at 360 nm, and for chitosan at 359 nm. The UV results obtained for glucose, chitosan and green tea are in agreement with the corresponding TEM results obtained which showed that the particles have an average size of 8–31 nm. However, the results obtained for ascorbic acid are not in agreement, since the corresponding TEM result showed that the particles have an average size of 96 nm. The peaks were all blue shifted in relation to the bulk band gap of Ag_2Se-NPs (1033 nm), which indicated the formation of nanoparticles.

3.2 Photoluminescence studies

The photoluminescence properties of Ag_2Se nanoparticles were also studied using various excitation wavelengths

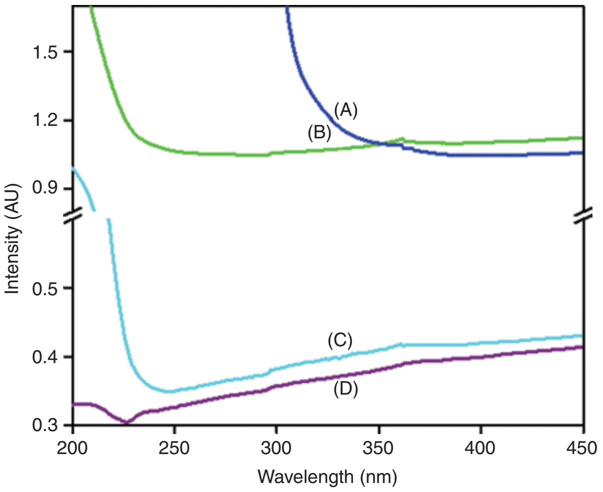

Figure 1: Absorption spectra of Ag_2Se nanoparticles capped with (A) green tea, (B) glucose, (C) chitosan and (D) ascorbic acid.

(240–550 nm). Figure 2 shows the photoluminescence spectra of Ag_2Se nanoparticles at room temperature. The figure shows two kinds of emission peaks with an increase in excitation wavelength. The first kind of peaks is sharp and showed an increase in emission wavelength with an increase in excitation wavelength. This is called moving emission (ME). In addition there are two rows of this kind of emission where one row changes the emission from 240 nm to 330 nm and the other alters it from 390 nm to 550 nm. The intensity of ME is also changing with an increase in excitation wavelength and reached its highest intensity at 270 nm. The second kind of peaks is broad and keeps its position as the excitation wavelength increases. This kind is called standing emission (SE). When the applied excitation was 450–550 nm, the SE peak disappeared. The behavior of ME and SE corresponds to the increase in excitation wavelength which indicated that they are dependent on the excitation wavelength [14].

FTIR analysis was conducted in order to determine the molecular interactions between the capping agents and the silver selenide nanoparticles (Ag_2Se-NPs). The spectrum of pure glucose showed an O-H stretch at 3407 cm^{-1}, CH_2OH side chain at 1250 cm^{-1}, C-O, C-C stretch at 1146 cm^{-1}, and C-O-C stretch at 989 cm^{-1}. After the reaction of Ag_2Se-NPs

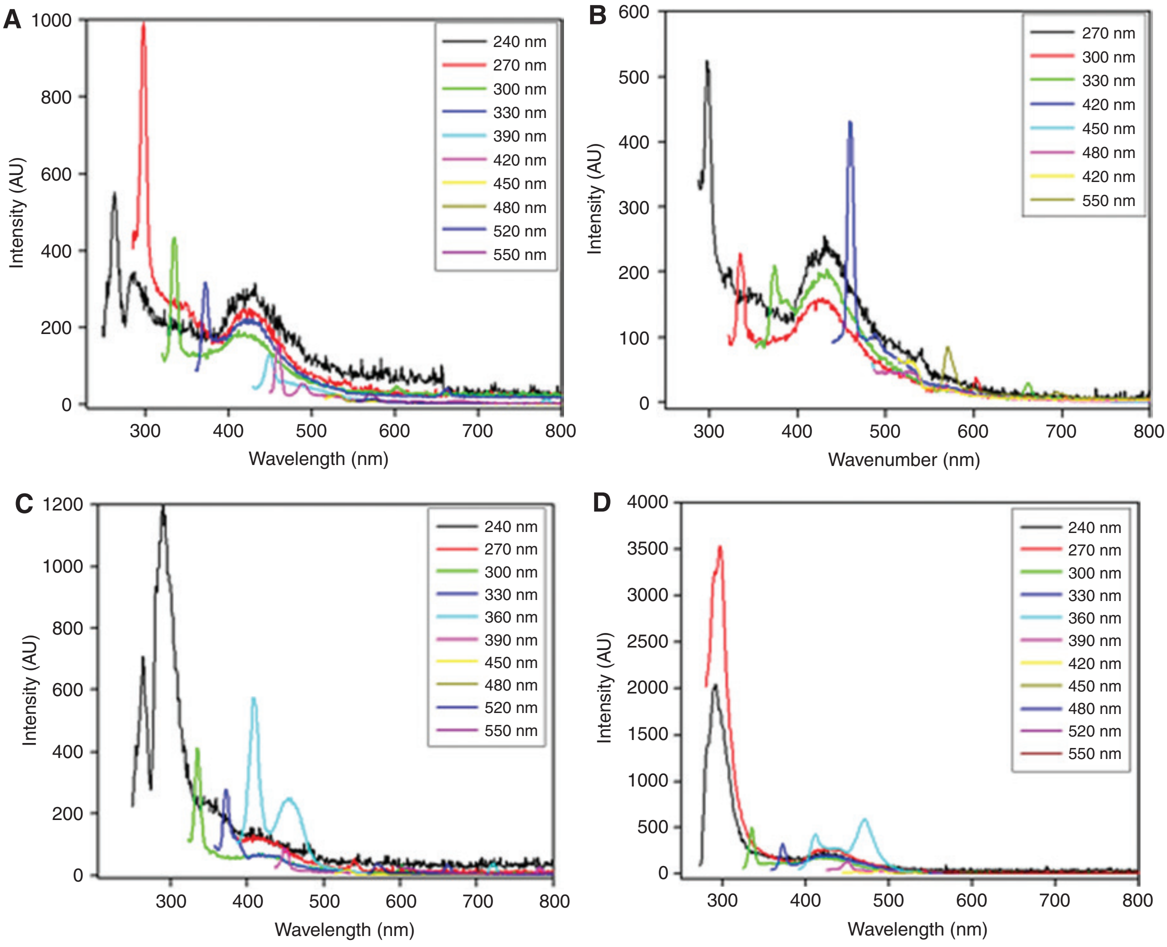

Figure 2: Emission spectra of Ag_2Se nanoparticles capped with (A) green tea, (B) glucose, (C) ascorbic acid and (D) chitosan.

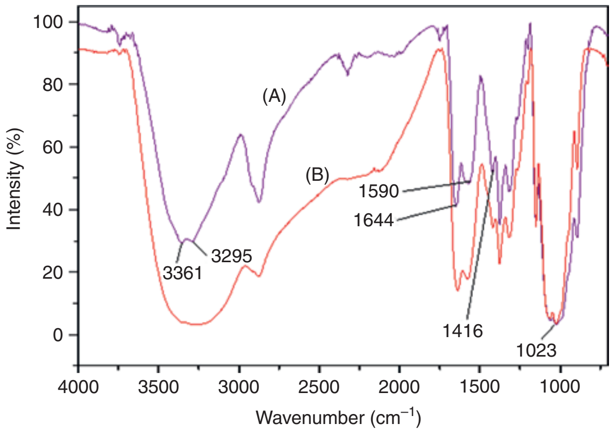

Figure 3: Fourier transformer infrared (FTIR) spectra of (A) pure chitosan and (B) chitosan capped silver selenide nanoparticles.

the O-H stretch shifted to 3565 cm^{-1}, CH$_2$OH side chain at 1219 cm^{-1}, C-O, C-C stretch to 1147 cm^{-1}, and C-O-C stretch to 988 cm^{-1} [2]. The spectrum of pure green tea showed an O-H stretch at 3562 cm^{-1} and 3737 cm^{-1}, a C=C stretch at 1520 cm^{-1}, a C-O-C stretch at 1236 cm^{-1} and a C-O stretch at 1058 cm^{-1}. These peaks showed a shift after the reaction with Ag$_2$Se-NPs to 3745 cm^{-1}, 1535 cm^{-1}, 1228 cm^{-1} and 1003 cm^{-1}, respectively. The presence of these functional groups on green tea capped Ag$_2$Se-NPs confirmed a successful capping of the nanoparticles by green tea [15]. The spectrum of pure ascorbic acid showed an O-H stretch at 2719 cm^{-1}, and a stretching vibration at 1655 cm^{-1}, which is due to a C=C bond. It also showed a peak at 1322 cm^{-1} which is due enol hydroxyl. After the reaction with nanoparticles, the peak due to an O-H stretch shifted to 2665 cm^{-1}. The peak at 1655 cm^{-1} disappeared and a peak at 1782 cm^{-1} was observed which is due to an ester carbonyl group. The peak at 1322 cm^{-1} shifted to 1362 cm^{-1}. These findings confirmed the presence of a poly hydroxyl structure of ascorbic acid on the surface of Ag$_2$Se-NPs [16]. The spectrum of chitosan capped silver selenide nanoparticles showed transmissions at 3361 cm^{-1} and 3295 cm^{-1} assigned to the overlap of O-H and N-H stretching vibrations. The band at 2871 cm^{-1} corresponds to C-H stretching, at 1644 cm^{-1} and 1590 cm^{-1} to -NH$_2$ bending, at 1416 cm^{-1}, 1374 cm^{-1} and 1315 cm^{-1} to C-H bending and at 1023 cm^{-1} to -C-O skeletal stretching. This trend was also observed in the chitosan capped Ag$_2$Se-NPs spectrum (Figure 3). A shift in bands was noticed (from 3361 cm^{-1} to 3341 cm^{-1}, 3295 cm^{-1} to 3284 cm^{-1}, 1644 cm^{-1} to 1639 cm^{-1}, 1590 cm^{-1} to 1589 cm^{-1}, 1416 cm^{-1} to 1419 cm^{-1}, 1374 cm^{-1} to 1375 cm^{-1}, 1315 cm^{-1} to 1320 cm^{-1} and 1023 cm^{-1} to 1013 cm^{-1}) [7]. Also, an increase in the sharpness of the peaks was observed in the chitosan capped nanoparticles. These observations indicated the interaction between the Ag$_2$Se-NPs surface and the chitosan amino and hydroxyl groups. This then suggests that NPs were capped by the chitosan.

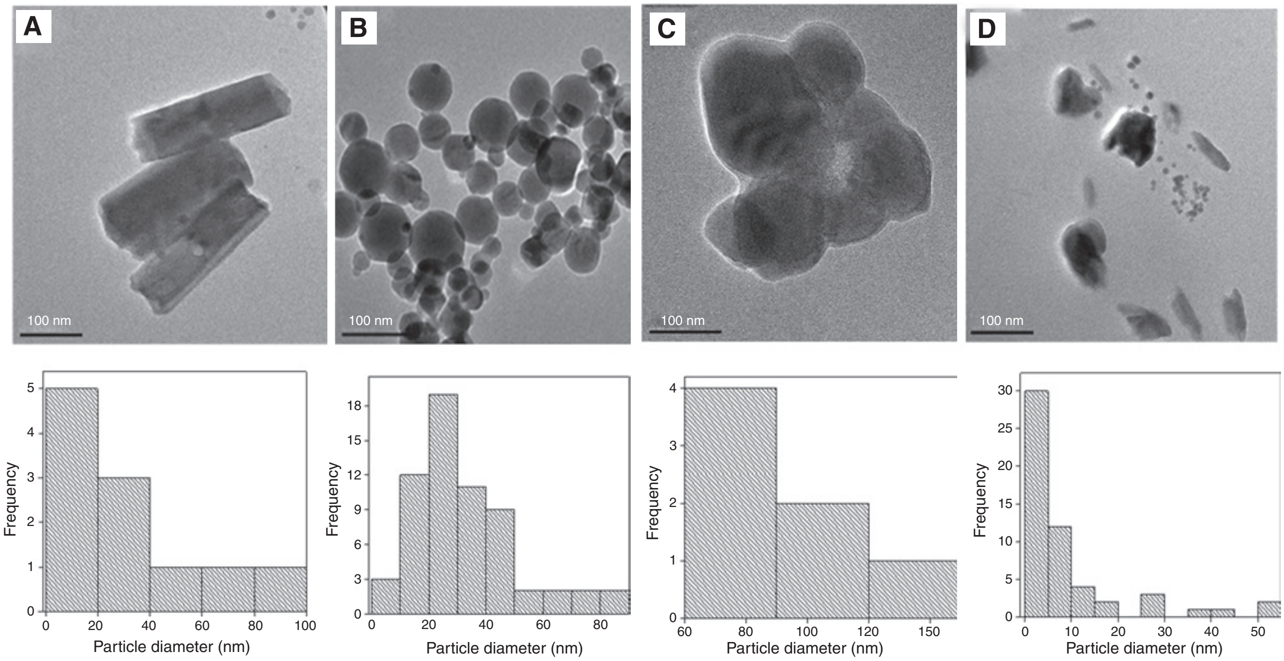

Figure 4: The transmission electron microscopy (TEM) micrographs and size histograms of Ag$_2$Se nanoparticles capped with 1.0% (w/v) of (A) green tea, (B) glucose, (C) ascorbic acid and (D) chitosan.

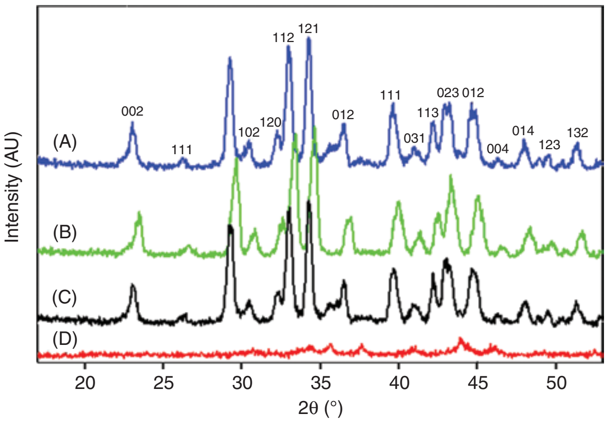

Figure 5: The X-ray diffraction (XRD) patterns of Ag_2Se nanoparticles capped with 1.0 % (w/v) of (A) green tea, (B) glucose, (C) ascorbic acid and (D) chitosan.

3.3 Morphological analysis

TEM was used to investigate the effect of capping agents on the size and shape of Ag_2Se nanoparticles. TEM micrographs and size histograms of Ag_2Se nanoparticles capped with green tea, glucose, ascorbic acid and chitosan are shown in Figures 4A–D. All the capping agents investigated gave mixed shapes of nanoparticles. Chitosan gave the smallest size, while ascorbic acid gave the biggest size of nanoparticles compared to the other capping agents studied. The reason could be that chitosan has the ability to chelate metals and can form various chemical bonds with metal components, thus enhancing the stability of the nanoparticles [7]. Green tea capped Ag_2Se nanoparticles gave spherical and rod shapes with an average size 30 nm. Glucose capped nanoparticles gave spherical and cubic shapes with an average size of 31 nm. Ascorbic acid capped nanoparticles gave spherical shape with average size of 96 nm. Chitosan capped nanoparticles gave spherical and rod-like shaped nanoparticles with an average size of 8 nm. Chitosan capped copper nanoparticles have been synthesized and spherical nanoparticles with a mean size of 35–75 nm were obtained [7]. Jafari et al. [1] prepared Ag_2Se nanoparticles using KSN as a complexing agent and hydrazine as a reducing agent, and spherical nanoparticles with less than 50 nm diameter were obtained. Oluwafemi and Revaprasadu [13] synthesized ascorbic acid capped CdSe nanoparticles and obtained spherical nanoparticles. Energy dispersive X-ray detection also confirmed the presence of Ag and Se in a 2 : 1 ratio in the synthesized nanoparticles, which corresponds with the formula Ag_2Se.

Figure 5 shows the X-ray diffraction patterns of the synthesized Ag_2Se nanoparticles which can be indexed to the ß-phase Ag_2Se (JCPDS card no. 201041), with the presence of (002), (013), (004) and (014) peaks charactering the orthorhombic phase. All capping agents gave the same diffraction patterns, which indicate that there is no effect observed on the phase of nanoparticles that was due to capping agent. The (111) plane indicates the presence of silver in the face centered cubic phase. The sharpness of peaks indicates the high degree of crystallinity of the nanoparticles.

Thermogravimetric analysis (TGA) was used to study the decomposition temperature and stability of the nanoparticles. A TGA thermograph of silver selenide nanoparticles with chitosan capping agent showed two degradation steps, while green tea, glucose and ascorbic acid showed

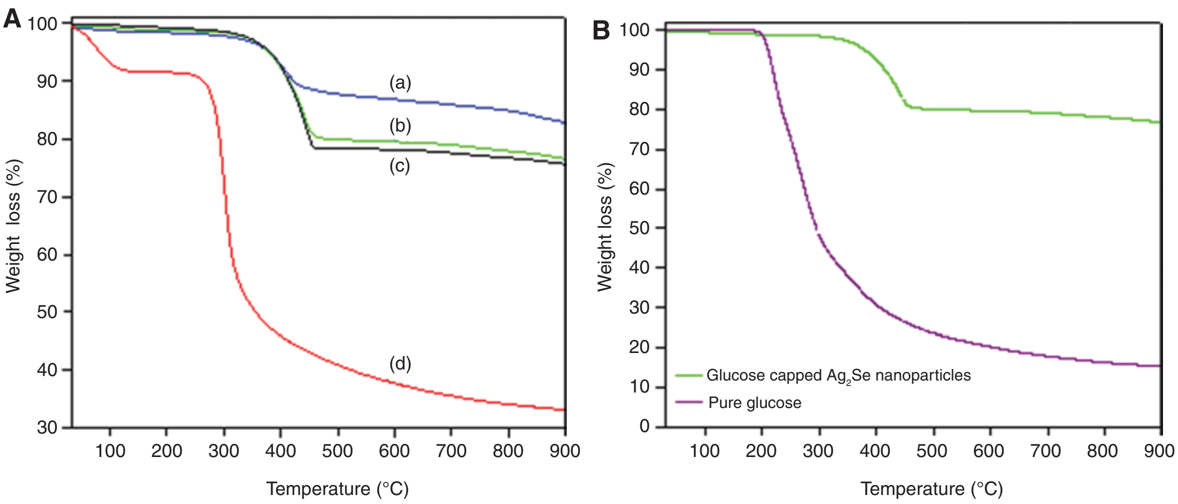

Figure 6: (A) Thermogravimetric analysis (TGA) graph of Ag_2Se nanoparticles capped with green tea (a), glucose (b), ascorbic acid (c) and chitosan (d). (B) glucose capped nanoparticles and pure glucose.

one step as shown in Figure 6A. The degradation around 100°C for chitosan capped nanoparticles was due to water desorption from the nanoparticles. Green tea, glucose, ascorbic acid and chitosan capped nanoparticles showed degradation with weight loss at 409°C (16%), 450°C (23%), 445°C (24%) and 284°C (67%), respectively. These degradation steps were due to the degradation of the capping agent leaving the silver selenide nanoparticles behind. The TGA thermogram showed no further weight loss, which indicated a high thermal stability of the synthesized pure silver selenide nanoparticles. The TGA showed the stability of the capping agents in the following order: green tea > glucose > ascorbic acid > chitosan. The degradation temperature of the capped Ag_2Se nanoparticles was higher than that of the capping agents alone, while the weight loss was lower for the capped nanoparticles than the capping alone, as shown in Figure 6B. This difference was influenced by nanoparticles residue which indicates that the nanoparticles without the capping agent can remain intact at higher temperatures.

4 Conclusion

The silver selenide nanoparticles were successfully prepared and capped with green tea, glucose, ascorbic acid and chitosan. The XRD study confirmed that the synthesized nanoparticles are orthorhombic β-phase Ag_2Se. TEM analysis showed that the nanoparticles have a mixture of sheets, spherical, rod and cubic shapes with an average size of 8–96 nm depending on the capping agent used. Different capping agents gave different sizes and shapes, which indicated that the capping agent has an influence on the size and shape of the nanoparticles.

Acknowledgments: The authors thank the Vaal University of Technology (VUT) research directorate and the Department of Chemistry for funding, laboratory support and research infrastructure used for carrying out the research work.

References

[1] Jafari M, Salavati-Niasari M. *Nanomater. Appl. Prop*. 2013, 2, 1–3.
[2] Oluwafemi OS, Revaprasadu N. *Mater. Res. Soc. Symp. Proc*, 2009, 1138, 12–19.
[3] Sajanlal PR, Sreeprasad TS, Samal AK, Pradeep T. *Nano. Rev.* 2011, 2, 58–83.
[4] Vidhya K, Saravanan M, Bhoopathi G, Devarajan VP, Subanya S. *Appl. Nanosci.* 2015, 5, 235–243.
[5] Shakouri-Arani M, Salavati-Niasari M. *Spectrochim. Acta, Part A* 2014, 133, 463–471.
[6] Salavati-Niasari M, Davar F, Loghman-Estark MR. *J. Alloys Compd.* 2009, 481, 776–780.
[7] Usman MS, Ibrahim NA, Shameli K, Zainuddin N, Yunus WMZM. *Molecules* 2012, 17, 14928–14936.
[8] Zain MN, Stapley AGF, Shama G. *Carbohydr. Polym*. 2014, 112, 195–202.
[9] Senapati US, Jhaand DK, Sarkar D. *Res. J. Phys. Sci.* 2013, 1, 1–6.
[10] Nadagouda MN, Varma RS. *Green Chem.* 2008, 10, 859–862.
[11] Dang TMD, Le TTT, Fribourg-Blancand E, Dang MD. *Adv. Nat. Sci.: Nanosci. Nanotechnol.* 2011, 2, 015009 (6 pp).
[12] Ansari F, Bazarganipour M, Salavati-Niasari M. *Mater. Sci. Semicond. Process* 2016, 43, 34–40.
[13] Oluwafemi OS, Revaprasadu N. *Mater. Lett*. 2012, 75, 84–86.
[14] De-Sheng X, Yu G, Wen-Jing L, Ming-Su S, Zai-Wen L. *Chin. Phys. Lett*. 2007, 24, 1756–1758.
[15] Reddy NJ, Vali DN, Rani M, Rani SS. *Mater. Sci. Eng. C* 2014, 34, 115–122.
[16] Xiong J, Wang Y, Xue Q, Wu X. *Green Chem.* 2011, 13, 900–904.

Bionotes

Nokwethemba Precious Sibiya

Nokwethemba Precious Sibiya is an analytical chemistry lecturer and researcher. Her research focus is on synthesizing a variety of nanoparticles with improved antibacterial activity using greener, sustainable environmentally friendly methods in order to develop new and/or improved antibiotics. She is also interested in working on the removal of organic compounds in environmental samples (water and sediments).

Makwena Justice Moloto

Makwena Justice Moloto is currently an associate professor and acting head of the Department of Chemistry, Vaal University of Technology. He has published about 40 peer reviewed articles in his research area of inorganic nanochemistry and polymer chemistry. His research interest lies in the study of semiconductor nanoparticles, their incorporation in polymer fibers and various explorations of their biological, biomedical applications and water treatment. He serves as a reviewer for a number of international materials and nanotechnology journals.