

HEXADECYLAMINE-CAPPED SILVER SELENIDE NANOPARTICLES: TEMPERATURE STUDY

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Morphology control of nanoparticles has been the subject of great interest for modifying the properties of materials. Capping agents or organically capping molecules are also known to influence the particle growth and stability giving rise to different shapes and sizes. In this work, Ag₂Se nanoparticles were synthesized using HDA as capping agent in the temperature range of (130-190 °C). The prepared nanoparticles were synthesized using the metal organic route method by the interaction of selenium powder and silver nitrate in the presence of trioctylphosphine as solvent and characterized with UV-Vis spectrometry and photoluminescence for optical properties, transmission electron microscopy (TEM) for shape and size and X-ray powder diffraction (XRD) for structural analysis. The absorption spectra of all three samples show a blue shift from the bulk of the material. The TEM images show that uniform monodispersed spherical shape nanoparticles were obtained with the size distribution ranging from 4 to 12 nm for 130 °C, 4 to 16 nm for 160 °C and 4 to 18 nm for 190 °C. The X-ray diffraction results showed peaks which were identified as due to α -Ag₂Se body centered cubic compound. Some evidence of impurities were observed in the XRD analysis of all the three temperatures and indexed to metallic silver in the face centered cubic.

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1. Introduction

Nanoparticles with different morphologies are of great interest because different particle shapes can bring in electronic, optical and magnetic properties which are different from their spherical counterparts [1]. Morphology control of nanoparticles is the one that many researchers are focusing on, and has been the subject of great interest in terms of modifying their materials properties. Semiconducting nanoparticles of various shapes like (triangles, rods, cubes, arrows and tetrapods) [2], have been produced by solution methods employing appropriate capping molecules, since capping molecules are also known to influence the particle growth and stability giving rise to different shapes and sizes. The size and shape of the nanoparticles can be tuned by changing the concentration of the capping molecules. Therefore the study of size and shape effect on the material properties is of importance for scientific understanding as well as tailoring the application of those materials. In many semiconductors, decreasing the size of the material can provide a way to tune the physical properties and observe new phenomena.

Silver selenide is a member of silver chalcogenide, and it belongs to the group I–VI semiconductor materials with the optical band gap of 1.2 eV [3]. Silver selenide is found to exhibit only n-type semiconducting property at 4.2K even with 0.37% excess selenium [4]. It has been reported to be a very good ionic conductor at room temperature and behaves as a magneto-resistive material upon alternation of stoichiometry between respective elements[4][5]. Silver selenide has been extensively studied in literature due to its many interesting and useful properties[6]. Silver

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selenide (Ag_2Se) undergoes a phase transition at 133°C . Its high temperature phase ($\beta\text{-Ag}_2\text{Se}$, $>133^\circ\text{C}$) is a well known superionic conductor that has been utilized as the solid electrolyte in photochargeable secondary batteries [7]. The low temperature phase ($\alpha\text{-Ag}_2\text{Se}$, $<133^\circ\text{C}$) is a nonmagnetic, narrow band gap semiconductor which has been widely used as a photosensitizer in photographic films or thermochromic materials [8]. $\alpha\text{-Ag}_2\text{Se}$ is also a promising candidate for thermoelectric applications because of its relatively high Seebeck coefficient ($-150\mu\text{V K}^{-1}$ at 300K), low lattice thermal conductivity, and high electrical conductivity [9]. A large magnetoresistance has also been reported for a nonstoichiometric derivative of this solid [10]. Jeong and Xia have reported that the reversible phase transition associated with Ag_2Se provides a new platform for the fabrication of photonic crystals with thermally switchable stop bands [11]. Qian et al reported a hydrothermal approach to Ag_2Se nanocrystals that used silver nitrate and elemental selenium as precursors [12]. Xia et al has shown a procedure for the synthesis of Ag_2Se nanocrystals in pyridine via the reaction of AgNO_3 and selenium with KBH_4 or in ethylenediamine through sonochemical activation [13]. Various methods were used for the synthesis of silver selenide nanoparticles. Here we report the synthesis of HDA-capped Ag_2Se nanoparticles using the method reported by Bawendi et al [14]. This method is faster and easier in terms of controlling the size and shape of the nanoparticles. The study is intended to achieve high quality silver selenide nanoparticles which could lead to new applications or could significantly improve the performance of existing applications. The effect of temperature variation was investigated for the formation of silver selenide nanoparticles.

2. Experimental details

2.1 Materials

Silver nitrate (99%), selenium powder (99.5%, 100 mesh), tri-n-octylphosphine (TOP) and hexadecylamine (HDA) (90%) were purchased from Sigma – Aldrich. Methanol and toluene were obtained from CC Immanuel. All chemicals were used without further purification.

2.2 Instrumentation

The optical measurements were carried out using Perkin-Elmer Lambda 25 UV/VIS spectrophotometer (ELICO-SL-150). The samples were placed in quartz cuvettes (1 cm path length) using toluene as a reference solvent. A Perkin Elmer LS 45 was used to measure the photoluminescence of the particles at the excitation wavelength of 200nm. The nanoparticles were dissolved in toluene and placed in glass cuvettes (1 cm path length) for analysis. The TEM images were recorded using HITACHI JEOL 100S transmission microscope operated at 80kV. The nanoparticles were prepared by first diluting them with toluene, and placing a drop of diluted sample on a carbon-coated copper grid and drying at room temperature. The powder X-ray diffraction patterns were recorded by a BRUKER D2 diffractometer at 40kV/50mA using secondary graphite monochromated $\text{Co K}\alpha$ radiation ($\lambda = 1.7902$). Measurements were taken at high angle 2θ range of ($5 - 90^\circ$) with a scan speed of 0.01°s^{-1} .

2.3 Synthesis

2.3.1 Synthesis of Ag_2Se nanoparticles

In the preparation of Ag_2Se nanoparticles, selenium powder (0.5 g) and AgNO_3 (0.5 g) were dissolved separately with 5ml tri-n-octylphosphine (TOP) to obtain the solution of TOP-Se and TOP-Ag respectively. The prepared TOP-Se was then injected into a hot HDA (6 g) followed by TOP-Ag at a specific reaction temperature ($130, 160$ and 190°C) under the flow of nitrogen gas. The reaction resulted in a dark brown solution. The solution was stirred for 1 hour and cooled to about 70°C . The Ag_2Se nanoparticles were precipitated with an excess methanol and separated by centrifuge. The particles were washed with methanol and redispersed in toluene. The growth of Ag_2Se nanoparticles were studied by varying the effect of temperature.

3. Results and Discussion

HDA-capped Ag_2Se nanoparticles have been reported before using method to produce good uniform shape while particle size distributions showing good size control of the particles. Ng et al [15] used the method called single source precursor to synthesize HDA-capped Ag_2Se nanoparticles whereby silver(i)selenocarboxylate were used as precursors. Mlambo et al [16] synthesized HDA-capped Ag_2Se nanoparticles using colloidal route method whereby Se powder was reduced by sodium borohydride (NaBH_4) to give selenium ions and silver nitrate (AgNO_3) were used as a source for Ag. In this paper we report about using AgNO_3 and Se powder with TOP to generate better control of particles in a hot boiling HDA. In our study TOP was used as a reducing agent and as a solvent to dissolve the precursors. The metal organic route method was used for the synthesis of HDA-capped Ag_2Se nanoparticles.

3.1 Effect of temperature

3.1.1 Optical properties

Silver selenide nanoparticles were synthesized using HDA as a capping agent. The effect of temperature was investigated in HDA-capped Ag_2Se nanoparticles. The temperature variation was performed during this experiment to check the effect of temperature on the formation of nanoparticles in terms of size and shape. The effect of temperature was investigated by varying the temperature from 130, 160 and 190°C.

Figure 1 (a) and (b) shows absorption and emission spectra of HDA-capped Ag_2Se nanoparticles synthesized at different temperatures (130, 160 and 190°C). The absorption spectra in Figure 1 (a) shows a blue shift from the bulk band gap of 1035nm with the band edge increasing as the temperature increases. Figure 1 (a) (i) show a blue shift from the bulk with the band edge of 284 nm. At higher temperatures of (160 and 190° C) in Figure 1 (a)(ii) and (iii) an increase in the absorption band edges were observed at about 290 and 330 nm respectively indicating change in relation to their particle size with temperature increase. The growth of the particle size was observed due to Ostwald ripening. Figure 1 (b) shows emission peaks which were all red shifted from their corresponding absorption band edges. Figure 1 (b) (i) and (ii) show a slight shift from the lower wavelength to the higher wavelength as the temperature was increased from 130°C (424 nm) to 160°C (425 nm). As the temperature was further increased to 190°C in Figure 1 (b)(iii) there was a slight decrease towards the lower wavelength of 423 nm and this could be due to the change in morphology of the particles forming small crystal at higher temperature with increased particles size and this is confirmed by TEM image in Figure 2 (e). The reaction favoured thermodynamic rather than kinetics since the most stable form of nanocrystals with spherical shaped were formed when temperature was increased from 130 to 190 °C with an increased particle size as observed in the TEM.

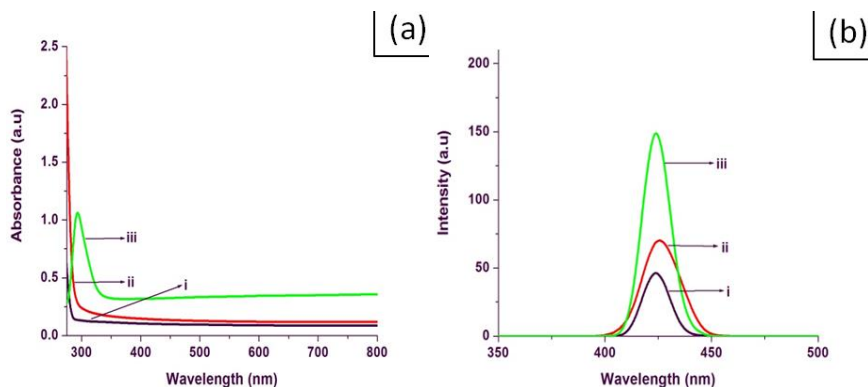


Fig. 1: (a) Absorption and (b) emission spectra of HDA-capped Ag_2Se nanoparticles prepared at different temperatures (i) 130°C, (ii) 160°C and (iii) 190°C

3.1.2 Structural characterization

The TEM images in Figure 2 show HDA-capped Ag_2Se nanoparticles prepared at different growth temperatures of (130, 160 and 190°C). The TEM images for all the temperatures showed highly monodispersed spherical nanoparticles with the highest frequency of particles. The diameter of these nanoparticles increases with an increase in temperature. The TEM image in Figure 2 (a) show uniform, spherical particles were observed at 130°C for HDA-capped Ag_2Se nanoparticles with the particle size distribution of 2 to 12 nm as shown in Figure 2 (b). When the injection temperature was increased to 160°C uniform spherical shapes were also observed with the size distribution ranging from 4 to 16 nm as shown in Figure 2 (c) and (d). As the temperature was further increased to 190°C the nanoparticle sizes also increased with the size distribution ranging from 4 to 18 nm as shown in Figure 2 (e) and (f). This increase in nanoparticle sizes is as a result of Ostwald ripening. Ng et al. [15] have studied the effect of HDA on the morphology of nanoparticles at high temperature and they found that nanoparticles prepared with high amine concentration at high temperature are mainly small faceted crystals since more nuclei were produced under those conditions.

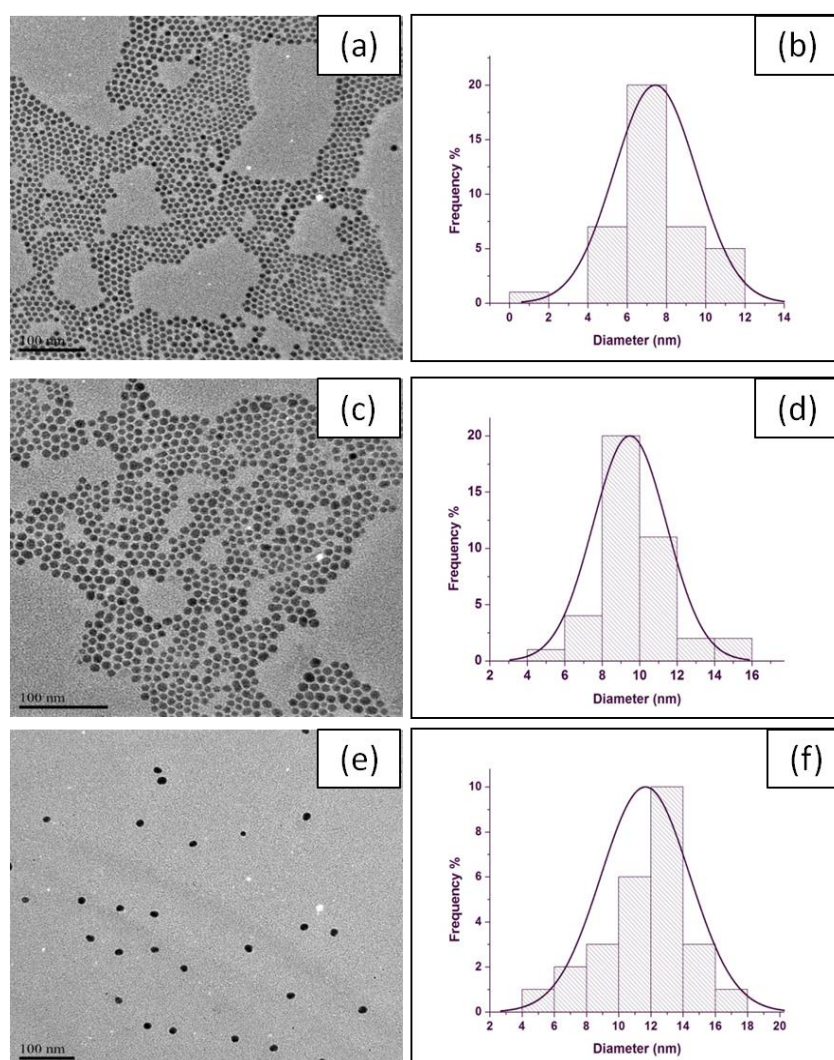


Fig. 2: TEM images of HDA-capped Ag_2Se nanoparticles prepared at different temperatures (a, b) 130°C, (c, d) 160°C and (e, f) 190°C

The XRD patterns shown in Figure 3 (a), (b) and (c) represent HDA-capped Ag_2Se nanoparticles prepared at different temperatures (130, 160 and 190°C). The peaks at $2\theta = 52.1^\circ$, 76.1° in Figure 3 (a) correspond to (200) and (222) planes confirming the body centered cubic α -

Ag_2Se (JCPDS, 01-076-0135). The sharp peak at $2\theta = 44.5^\circ$ correspond to (111) plane indicating the presence of silver in face centered cubic (JCPDS, 03-065-2871). The same peak at $2\theta = 44.5^\circ$ were observed for all the temperatures and it became more prominent as the temperature was increased from 130 to 190°C . Figure 3 (b) and (c) peaks correspond to (200) and (222) planes which also confirms the body centered cubic phase of α - Ag_2Se . The intensities of the peaks became more prominent for all the temperatures as the temperature was increased.

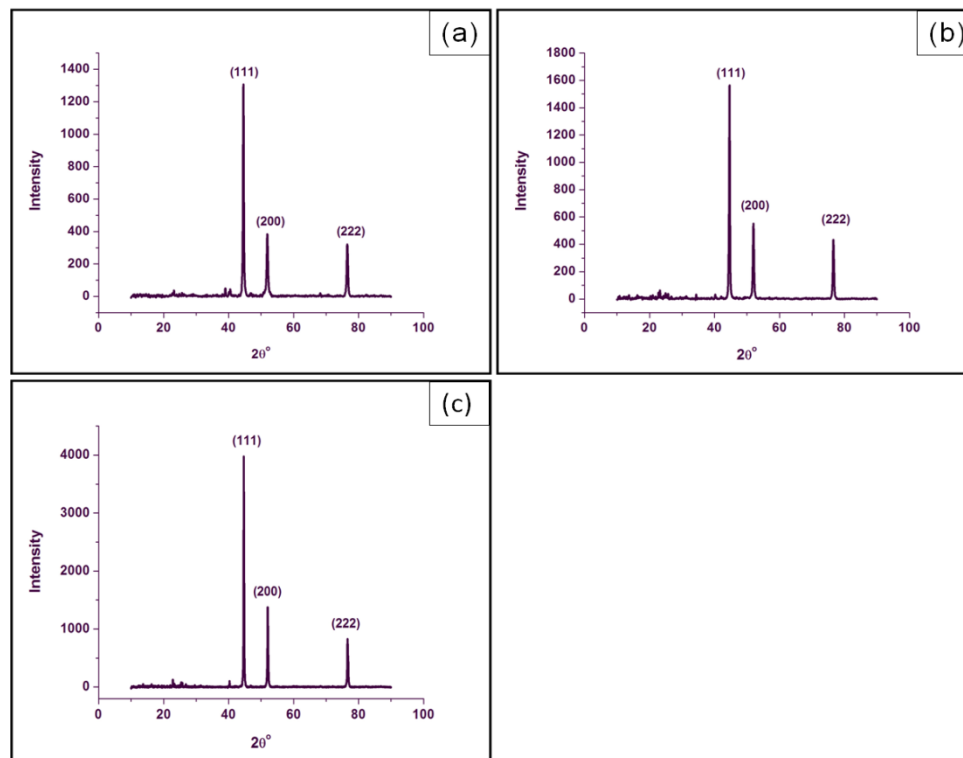


Fig. 3: XRD pattern of HDA-capped Ag_2Se nanoparticles prepared at different temperatures (a) 130°C , (b) 160°C and (c) 190°C .

4. Conclusions

HDA-capped Ag_2Se nanoparticles were prepared successfully using TOP-Ag and TOP-Se at various temperatures. The prepared particles seem to depend on the reaction temperature. The increase in temperature led to an increase in particle sizes. This increase in particle size was observed due to Ostwald ripening. The temperature variations were also found to influence the optical properties of silver selenide nanoparticles. The TEM results show uniform monodispersed spherical nanoparticles were obtained irrespective of temperature increase. The XRD showed peaks which were identified as due to α - Ag_2Se body centered cubic compound for all the temperatures. The sharp peak observed for all temperatures indicate the presence of silver in the face centered cubic.

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