

Silver and copper nanoparticles: Lower concentration controlled thermal decomposition of their salt precursors

D. S. More ^a, M. J. Moloto ^{b,*}

^a *Department of Biotechnology and Chemistry, Faculty of Applied and Computer Sciences, Vaal University of Technology, Private Bag X021, Vanderbijlpark, 1900, South Africa*

^b *Institute for Nanotechnology and Water Sustainability, College of Science, Engineering and Technology, University of South Africa, Florida Park, Roodeport, 1709, South Africa*

Generally, salt precursors have been investigated for the production of nanoparticles with semiconducting properties such as metal chalcogenides and others. They have demonstrated excellent features for the ease of converting them to nanoparticles. Thermal decomposition and solvothermal processes are often followed to produce particles with stabilizers of varied ranges of size with improved size control dependent on the set collective conditions and the intended applications. In this study, silver (Ag) and copper (Cu) nanoparticles were synthesized using the thermal decomposition method in the presence of oleylamine as a capping agent in order to produce good stable uniform monodispersed nanoparticles. Lower amounts of Ag and Cu precursors (0.1 - 0.2 g) were used to study their effect on the size and morphology of the nanoparticles. The synthesized nanoparticles under various conditions were characterized using UV/Vis and PL spectroscopy, TEM, and XRD. It was observed that an increase in the precursor concentration led to an increase in particle size with varying morphologies for both Ag and Cu nanoparticles. The TEM images of Ag nanoparticles showed that uniform morphology and spherical shape were observed with narrow diameters ranging from 5.9 to 6.8 nm. However, for Cu nanoparticles, uniform morphology and spherical shape were only observed at a precursor concentration of 0.15 g with an average diameter of 7.8 nm. The XRD results of both Ag and Cu nanoparticles showed peaks that were identified as Ag and Cu in the face-centred cubic.

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1. Introduction

Noble metal nanoparticles are the most studied in nowadays research because of their unusual physical and chemical properties which differ from their bulk material. They possess a very strong absorption in the visible region due to Surface Plasmon Resonance (SPR) which gives rise to such intense colors [1]. These properties are observed in metals such as silver (Ag), copper (Cu), and gold (Au). They show unique optical, electronic, mechanical, magnetic, and chemical properties because of their small sizes and large surface area [2]. Due to these properties metal nanoparticles have found application in areas such as catalysis [3], electronics [4], optics [5], and antimicrobial agents [[6, 7]. Previously, metal particles such as silver, copper, and zinc have been used for antibacterial applications because of their ability to penetrate the bacterial wall causing cell death or interacting with microbial cell membranes to cause the deactivation of their activity [8]. Among these metals, copper is one of the most unstable metals in dry air due to oxidation, but it can still be used in many applications because of its high conductivity and low cost. However, its synthesis in the air with controlled size and shape has been a major concern due to its high reactivity. On the other hand, one of the metals which have been extensively studied is silver which has also been widely used because of its highest electrical conductivity regardless of its

* Corresponding author: molotmj@unisa.ac.za
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high cost. The two metals (Ag and Cu) have similar chemical properties and their synthesis into nano-sized material can show enhanced or different properties when compared with their bulk material. To obtain particles with uniform size distributions, various methods have been used for the preparation of metallic nanoparticles such as metal salt reduction [9], microwave heating [10], sonochemical reduction [11], and thermal decomposition [12-15]. Among these methods, thermal decomposition is the most commonly used method to produce uniform, monodispersed nanoparticles. The synthesis of these nanoparticles was done using the thermal decomposition method in the presence of oleylamine which was used as a reducing/capping agent and a solvent that dissolved the precursors. This capping agent was chosen because of its low cost, readily available and less toxic when compared with other used alkylamines. Its usage as a ligand can be advantageous because of its weak interaction with the surface of the nanoparticles and can easily be displaced with hydrophobic and hydrophilic thiols on the surface of the nanoparticles in order to produce nanoparticles which are soluble in organic solvents or in water [16, 17]. Therefore, in this study, Ag and Cu nanoparticles were prepared in the presence of oleylamine and used as fillers in another study of composite nanofibers of which the paper has already been published. These nanoparticles have gained so much attention in research because of the properties they entailed such as a high surface to volume ratio and their small size which allows them to exhibit higher bactericidal activity over larger colloid forms and their bulk material [8]. The use of Ag and Cu nanoparticles especially in a mixture form can contribute to the lowering of cost relating to silver. In this study uniform, monodispersed and spherical particles were obtained with small sizes using just a single-step method using salt precursors. The synthesis of the metal nanoparticles were followed using modification from Chen et al. [18]. The component of this work was reported previously for the use of 0.15 g of the salt precursors used which were incorporated into the polymer matrices [19].

2. Experimental

2.1. Materials

The materials used includes the following: Silver nitrate (AgNO_3) (99%) analytical reagent AR grade, cupric oxalate, oleylamine technical grade 70%, ethanol and toluene. All chemicals were purchased from Merck (South Africa) and were used without purification.

2.2. Instrumentation

Optical characterization: The optical measurements were carried out using PerkinElmer Lambda 25 UV/VIS spectrophotometer (ELICO-SL-150). The samples were placed in quartz cuvettes (1 cm path length) using ethanol and toluene as a reference solvent for copper and silver, respectively. The samples were scanned from 900 to 200 nm to find the maximum absorbance and surface plasmon resonance (SPR) of Ag and Cu nanoparticles. A Perkin Elmer LS 45 fluorimeter was used to measure the photoluminescence of the particles at the excitation wavelength of 350 nm. The samples were placed in quartz cuvettes (1cm path length) for analysis. **Transmission electron microscopy (TEM):** The TEM images were recorded using HITACHI JEOL 100S transmission microscope operated at 80 kV. The nanoparticles were diluted in both ethanol and toluene, and a droplet of a solution was placed on a carbon-coated copper grid. The samples were dried at room temperature before analysis. **X-ray diffraction (XRD):** The powder X-ray diffraction patterns were recorded by a BRUKER D2 diffractometer operating at 40 kV/30 mA using secondary graphite monochromated $\text{Co K}\alpha$ radiation ($\lambda = 1.7902$). Measurements were taken at a high-angle 2θ range of $5-90^\circ$ with a scan step of 0.01° .

2.3. Procedure

2.3.1. Synthesis of Ag and Cu nanoparticles

This method for the synthesis of silver (Ag) nanoparticles was adopted from Chen et al. [18] with minor modification. In a typical experiment, (0.1, 0.15, 0.2 g) of AgNO_3 was added to 6 ml of oleylamine. The solution was then transferred into a three-neck round-bottom flask and refluxed for 1 hr under the flow of nitrogen gas at 180°C . After 1 hr, the reaction was stopped and

cooled to about 70°C. A large amount of absolute ethanol was added to the solution to precipitate the Ag nanoparticles formed. The resulting nanoparticles were separated by centrifugation at 12000 rpm for 10 min and washed three times with ethanol to remove the excess capping agent. The resulting nanoparticles were left to dry for further characterization [19]. The same procedure was used for the preparation of Cu nanoparticles using cupric oxalate as a precursor. The growth of Ag and Cu nanoparticles was studied by varying the effect of precursor concentration.

3. Results and discussion

Silver (Ag) and copper (Cu) nanoparticles were prepared using the thermal decomposition method. In this synthesis, silver nitrate was used as a precursor to prepare silver nanoparticles whereas cupric oxalate was used as the precursor for the preparation of copper nanoparticles. There have been reports on the synthesis of Ag and Cu nanoparticles but none of them used just one solvent and a single-step method to produce nearly monodispersed Ag and Cu nanoparticles. Chen et al. [16] reported on the preparation of Ag nanoparticles by thermal decomposition using an oleylamine-liquid paraffin system which involved the heating of AgNO₃, liquid paraffin and oleylamine for 2 hours at 180 °C and aged them for 8 hours at 150°C. Osterloh et al.[17] also reported on the synthesis of nearly monodispersed Ag nanoparticles by thermal reduction of Ag oleic acid in the presence of oleylamine whereby hexane was refluxed for 2 days before adding a mixture of Ag oleic acid and oleylamine. Salavati-Niasari et al. [20], synthesized Cu nanoparticles using thermal decomposition whereby copper oxalate [Cu(O₄C₂)]–oleylamine complex was first prepared at 140 °C for 60 min. Then the resulting complex solution was further injected into triphenylphosphine (TPP) at 240 °C for 45 minutes. All of these were time-consuming and solvent-wasting. In this study uniform, monodispersed and spherical particles were obtained with small sizes using just a single-step method with a reduced time and oleyamine as a capping agent and a solvent used to dissolve the precursor salts.

3.1. Effect of precursor concentration on the size and shape of Ag and Cu nanoparticles

3.1.1. Optical properties of Ag and Cu nanoparticles

Concentration is one of the major factors that influence the reaction rate, size and shape of the nanoparticles. Therefore, controlling the physical and chemical properties of metal nanoparticles depends upon the tuning of their size and shape, and it can only be achieved by varying the reaction parameters such as precursor concentration, capping agent, temperature and time. Previous reports have shown that metal nanoparticles display a distinct surface-plasmon resonance (SPR) which is known to be very sensitive to the metal size, shape, dielectric constant and the embedding medium [9, 11]. Jiang et al. [21] stated that increasing the precursor concentration increased the nanoparticle size because of the higher concentration of metal ions existing in the solution, causing the nucleation speed to increase and leading to more nuclei growth steps. In this study, the effect of precursor concentration on the size and shape of Ag nanoparticles was investigated and the results showed that upon variation of silver nitrate precursor concentration uniform, spherical particles with smaller sizes were obtained. The prepared Ag nanoparticles were analyzed using UV-Vis and PL spectroscopy, TEM and XRD.

Figure 1 (a) and (b) shows the absorption and emission spectra of Ag nanoparticles prepared at different precursor concentrations of (0.1, 0.15 and 0.2 g/ 6 mL of oleylamine). Figure 1(a) (i), (ii) and (iii) show an increase in the surface plasmon resonance (SPR) as the precursor concentration was increased from 0.1, 0.15 and 0.2 g with the SPR bands of 426, 428, and 435 nm, respectively. The increase in the particle sizes at higher concentrations was due to Ostwald ripening and was further confirmed by the TEM images in Figure 2. Jiang et al. [21] reported that increased AgNO₃ concentration results in more Ag⁺ ions in the system and, therefore, promotes the growth of Ag nanoparticles and the formation of larger particles. They further mentioned that these larger particles tend to agglomerate and cause the surface Plasmon resonance (SPR) to shift towards the lower energy level. This subsequently leads to the red shift towards the longer wavelengths due to the delocalized and sharing of electrons near each particle surface among the

neighboring particles [20]. The broad SPR band for higher precursor concentration indicates the presence of different particle sizes of Ag nanoparticles in the solution. The emission peaks in Figure 1(b) were all red-shifted from their corresponding absorption band. Figures 1(b) (i) and (ii) showed a shift in the emission peaks from 433 to 446 nm as the precursor concentration was increased from 0.1 to 0.15 g. The emission peak of the highest precursor concentration (Figure 1(b) (iii)) showed a shift towards the lower wavelength of 431 nm, which suggest a change in morphology of the particles forming large crystals with increased particles size, and this was also confirmed by the structural analysis in Figure 3(e).

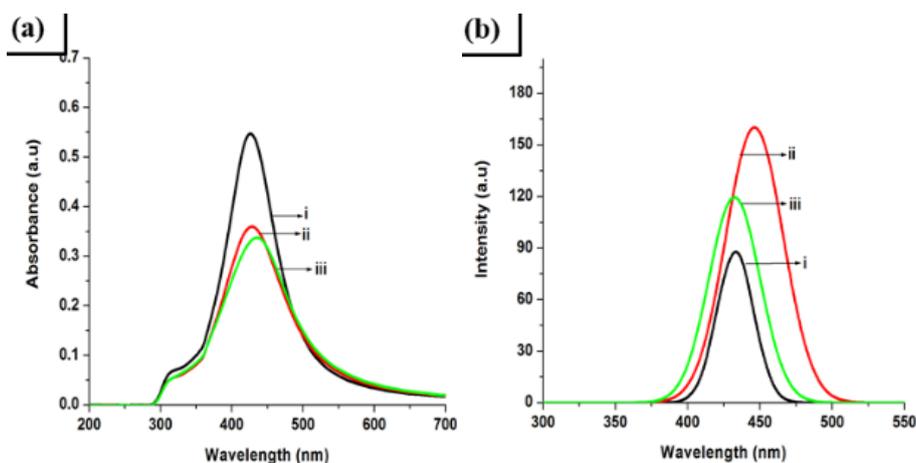


Fig. 1. Absorption (a) and Emission (b) spectra of Ag nanoparticles prepared at different precursor concentration (i) 0.1 g, (ii) 0.15 g and (iii) 0.2 g.

The synthesis of Cu nanoparticles was achieved by using the same method and conditions used for the preparation of Ag nanoparticles. This synthesis was accomplished by varying the precursor concentration in the range of 0.1, - 0.2 g of cupric oxalate. The effect of precursor concentration on the size and shape of the synthesized Cu nanoparticles was investigated.

Figure 2 (a) and (b) show absorption and emission spectra of Cu nanoparticles prepared at different precursor concentrations. The absorption spectra of Cu nanoparticles in Figures 2(a) (i), (ii) and (iii) showed an SPR peaks at 596, 601 and 617 nm. These peaks observed represent features of Cu nanoparticles, which are known to display an SPR band in the range of 350 – 800 nm [5, 6, 19]. According to the literature it was stated that the position of the SPR band for Cu nanoparticles is not known exactly and it can only be determined depending on parameters such as capping agent, type of solvent, size and shape of the particles [5, 6]. Other articles display the SPR band of Cu nanoparticles around 600 nm [7]. As observed, from the absorption spectra below show the SPR band increased with increasing the precursor concentration. It has been known that some metal nanoparticles display a distinct SPR in the visible region [8]. Figure 2(b) (i) (ii) and (iii) shows emission peaks which are red shifted from their corresponding absorption band with the values of 619, 624, and 623 nm for 0.1 g, 0.15 g [19] and 0.2g, respectively. There was a slight shift towards the lower wavelength when the precursor concentration was increased, signifying a change in morphology of the particles. This confirms to the TEM image and size distribution shown in Figures 4(e) and (f).

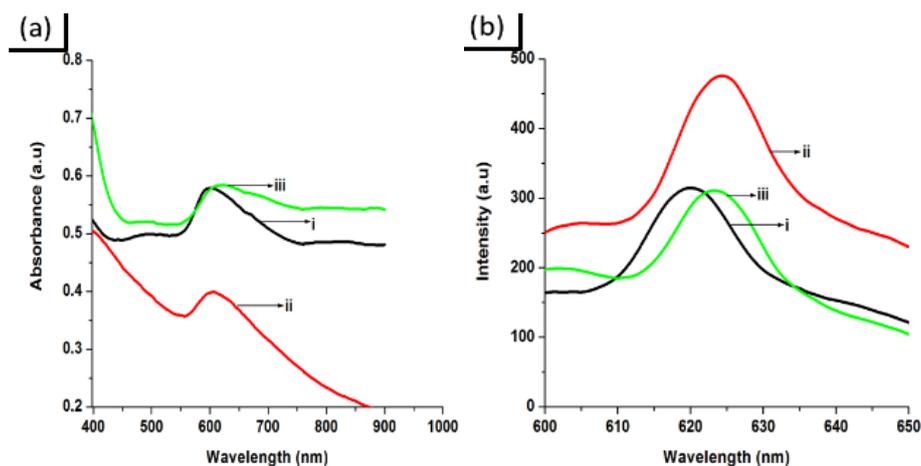


Fig. 2. Absorption (a) and emission (b) spectra of Cu nanoparticles prepared at different precursor concentrations (i) 0.1 g, (ii) 0.15 g, (iii) 0.2 g.

3.1.2. Structural characterization (TEM) of Ag and Cu nanoparticles

The TEM images and size distributions of silver nanoparticles prepared at different precursor concentrations of (0.1, 0.15 and 0.2 g / 6 mL oleylamine) are shown in Figure 3. It was observed that the particles in all the samples were of spherical shapes and their diameter increased with increasing the precursor concentration. However, the increase in particles size at the highest precursor concentration is a results of Ostwald ripening. Figure 3(a) shows that uniform, monodispersed and spherical particles were observed at lower precursor concentrations (0.1 g) with an average diameter of 5.9 nm as shown by the size distribution in Figure 3 (b). When the precursor concentration was raised to 0.15 g [19] uniform and spherical particles were also observed with an average particles size of 6.3 nm as shown in Figures 3(c) and (d). Furthermore, with an increase in the precursor concentration to 0.2 g, spherical particles were observed with an average particle size of 6.8 nm as shown in Figure 3(e). However, their distribution was not uniform and this was confirmed by the size distribution in Figure 3(f). Cheon et al. [22] reported that using higher precursor concentrations prolongs the time taken for the growth of the nanoparticles, thus resulting in varying morphologies. Ajitha et al. [23] also studied the effect of precursor concentration on the size of the nanoparticles and observed the dependence of particle growth on the concentration of the precursor. These results are in good agreement with the previous studies.

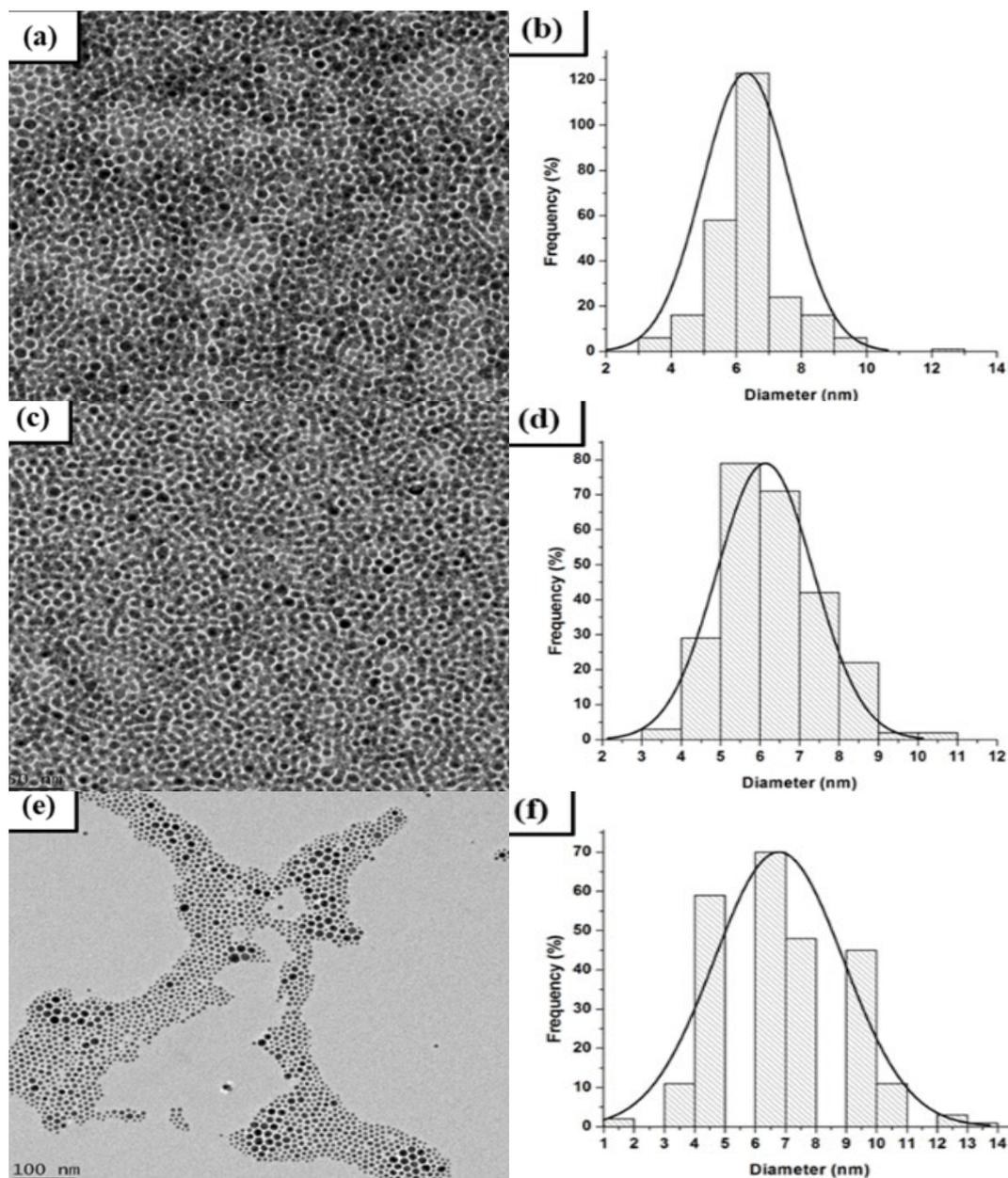


Fig. 3. TEM images and histograms of oleylamine-capped Ag nanoparticles prepared at different concentration (a, b) 0.1 g, (c, d) 0.15 g and (e, f) 0.2 g.

The TEM images in Figure 4 show Cu nanoparticles synthesized at different precursor concentrations. The particles were observed to be spherical however an increase in the precursor concentration caused agglomeration due to the rapid growth of the particles. Figure 4(a) [19] shows that the particles prepared at 0.1 g were very small and spherical with an average diameter of 2.4 nm as shown by the size distribution in Figure 4(b). When the precursor concentration was increased to 0.15 g, well-defined and spherical shape particles were observed with an average diameter of 7.8 nm as shown in Figures 4(c) and (d). As the precursor concentration was further increased to 0.2 g the nanoparticle sizes also increased forming larger crystals with an average diameter of 14.1 nm as shown in Figure 4(e) and (f). Peng et al. [24] conducted a study on the effect of precursor concentration on the size of the nanocrystals using the kinetics of the particle growth and observed that addition of precursor during the reaction yielded different size distribution of CdSe and InAs nanoparticles. The tailing of the absorption band and broadening of the PL are in agreement with the agglomeration of particles as observed in the TEM image.

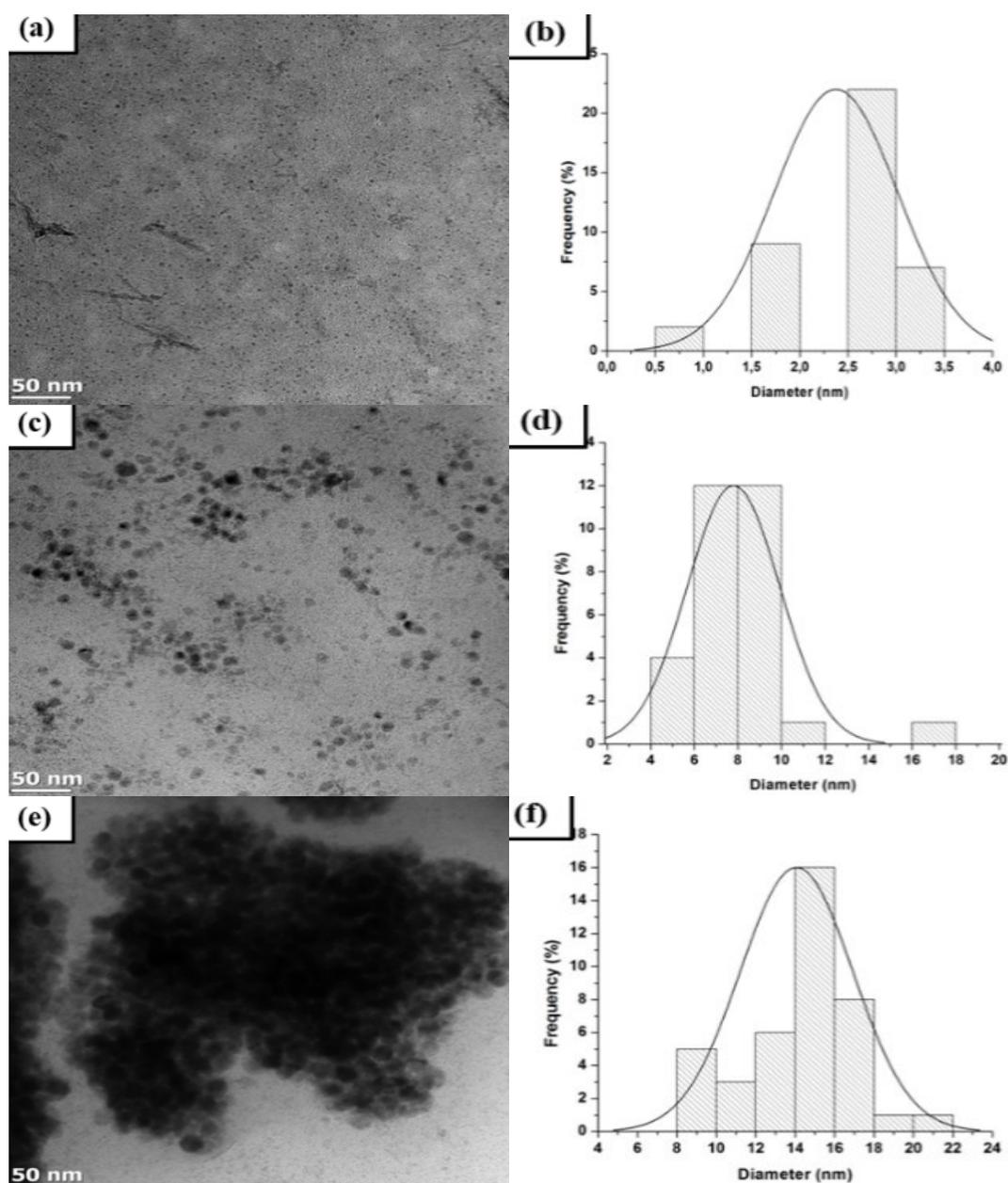


Fig. 4. TEM images and size distribution of oleylamine-capped Cu nanoparticles prepared at different concentrations (a, b) 0.1 g, (c, d) 0.15 g and (e, f) 0.2 g.

3.1.3. X-Ray diffraction (XRD)

The XRD patterns shown in Figure 5(i), (ii) and (iii) represent Ag nanoparticles prepared at different precursor concentrations (0.1, 0.15 and 0.2 g / 6 mL). The diffraction peaks at $2\theta = 44.3^\circ$, 51.7° and 76.1° correspond to (111), (222) and (220) planes for all the samples indicating metallic silver in the face-centered cubic (fcc) (JCPDS No, 03-065-2871). The intensity of the peak at $2\theta = 44.3^\circ$ became more prominent when the precursor concentration was increased. The broad peaks observed for all the three concentration confirms that the prepared Ag nanoparticles were of nanosized and highly crystalline. There was no evidence of impurities found in all the samples.

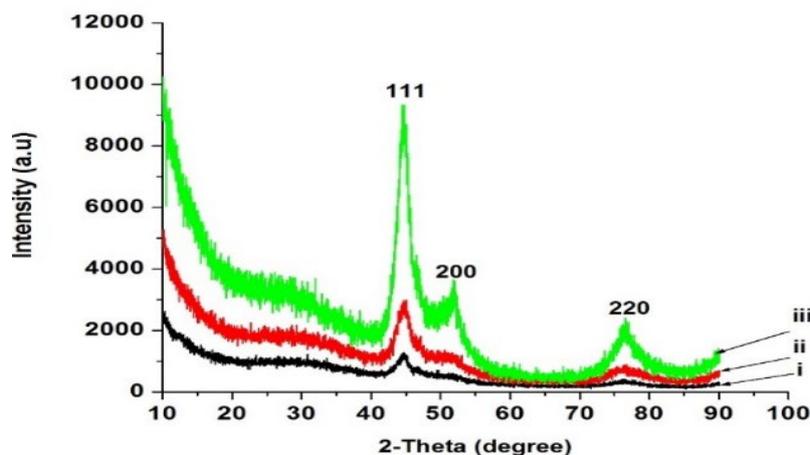


Fig. 5. XRD pattern of oleylamine-capped Ag nanoparticles prepared at different precursor concentration (i) 0.1 g, (ii) 0.15 g and (iii) 0.2 g.

The X-ray diffraction patterns of Cu nanoparticles synthesized at different precursor concentrations of (0.1, 0.15 and 0.2g / 6 mL of oleylamine) are shown in Figure 6(i), (ii) and (iii). The peaks at $2\theta = 43.2^\circ$, 50.7° and 74.2° for all the concentrations correspond to (111), (200) and (220) planes respectively, representing metallic copper in the face-centred cubic (fcc) structure. The peak position observed above is consistent with Bragg's reflections of the standard cubic structure of copper (JCPDS NO. 04-0836). Some evidences of impurities were observed for all the concentrations indicating the presence of Cu_2O in the sample due to oxidation in air.

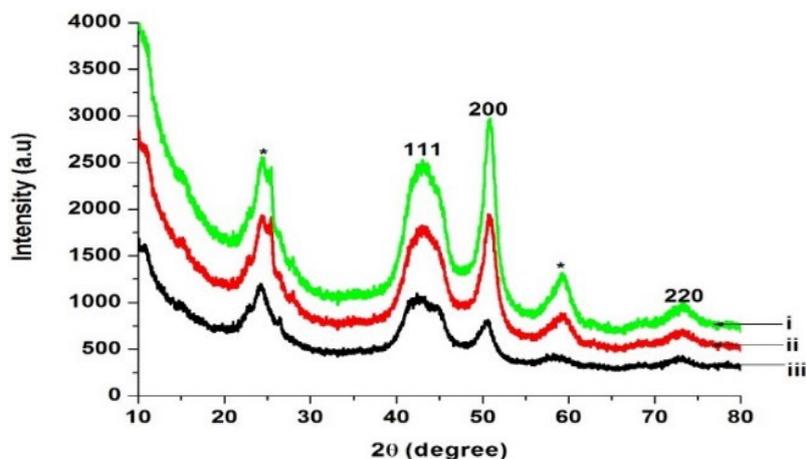


Fig. 6. XRD pattern of oleylamine-capped Cu nanoparticles prepared at different precursor concentration (i) 0.1 g, (ii) 0.15 g and (iii) 0.2 g.

4. Conclusion

Ag and Cu nanoparticles were both synthesized successfully by the thermal decomposition method using oleylamine as a capping agent. Both Ag and Cu nanoparticles were found to be affected by the precursor concentration variations. It is also evident that concentration plays an important role in the formation of Ag and Cu nanoparticles. The increase in the precursor concentration for Ag nanoparticles led to an increase in the particle size due to Ostwald ripening whereas for Cu nanoparticles larger particles were observed because of agglomeration. The tailing in the absorption band and broadening of the PL also confirmed the agglomeration of particles. Poor size distribution was observed for both Ag and Cu nanoparticles at high concentration. The

TEM images for 0.15 g/ 6 mL precursor concentration showed that uniform, monodispersed and spherical shape nanoparticles were observed with the average diameter of 6.3 nm for Ag and 7.8 nm for Cu nanoparticles. XRD analysis showed no evidence of impurities for Ag nanoparticles whereas for Cu nanoparticles there were impurities observed indicating the presence of Cu₂O in the sample. The absorption spectra of Ag nanoparticles often show the absorption bands between 400 – 450 nm whereas for Cu nanoparticles are observed in the range of 350 – 800 nm. The PL results for both Ag and Cu nanoparticles were all red-shifted from their corresponding absorption bands. The use of oleylamine as a reducing/capping agent gave better control of the nanoparticles with well-defined uniform and monodispersed Ag at all concentrations and Cu nanoparticles at a concentration of 0.15 g/ 6 mL.

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