Synthesis of silver nanoparticles by silver salt reduction and its characterization

Muhammad Muzamil, Naveed Khalid, M Danish Aziz and S Aun Abbas
NED University of Engineering & Technology, Karachi, Pakistan
E-mail: muzamil_vir@hotmail.com, naveed_nawab@hotmail.com, mdanishaziz@hotmail.com, aunabbas@live.com

Abstract. The wet chemical method route by metal salt reduction has been used to synthesize nanoparticles, using silver nitrate as an inorganic salt, aldehyde as a reducing agent and amino acid as a catalyst. During the reaction aldehyde oxidizes to carboxylic acid and encapsulates the silver nanoparticles to prevent agglomeration and provide barrier in the growth of particle. The existing work produces particles using lab grade chemical, here the presented work is by using industrial grade chemicals to make the process more cost & time effective. The nano silver powder has been studied for their formation, particle size, shape & compositional analysis using Scanning Electron Microscope (SEM) equipped with EDS. The particles size distributions were analyzed by Laser Particle Analyzer (LPA), structure & morphological analysis using x-ray diffraction (XRD) and Fourier-transform-infrared Spectroscopy (FTIR) confirmed the stabilization of particles by coating of carboxylic group. These studies infer that the particles are mostly spherical in shape and have an average size between 70 to 350 nm.

1. Introduction
In the Synthesis of Silver Nanoparticles, Top down & Bottom up are the two fundamental synthesis approaches for nanoparticles. Top down approach can be regarded as a process starting with a bulk material and then breaking it into small size. Typical processes include attrition, milling, lithography, mechanical & chemical manipulation tools [1].

The main advantages are universality and low cost. Even soft organic matter (e.g. grass) can be ground by first freezing it in liquid nitrogen. The main disadvantages are irregular surface structure, polydispersity of the final particles, and the introduction of many defects. The smaller the particle, the worse is the contamination.

In bottom up approach, organic & inorganic structures are created atom by atom, molecules by molecules, cluster by cluster. This technology synthesizes materials by from atomic or molecular species via by chemical reactions. In this way biological & chemical reactors create conditions for special growth and materials self-assembled together to form nano complex structure [1].

In this synthesization of silver nanoparticles the process is based on bottom up approach, which basically relies on the chemical reduction of metal salts, electrochemical pathways, or the controlled decomposition of metastable organometallic compounds in solution. Control over the growth of the primarily formed nanoclusters depends upon the rate of mixing, two extreme situations yield the desired monodispersity; ultrarapid mixing of very concentrated solutions, and ultraslow mixing of very dilute solutions, and their agglomeration is effected by the use of a variety of stabilizers, in the form of donor ligands, polymers, and surfactants [2].
In the precursors of process, propanal is known to be a weak reducing agent & it has no significant reducing effect on AgNO₃, metallic salt, in the absence of a catalyst such as diethyl amine (DEA). Without using DEA, propanal takes quarter of a day to reduce silver salt but in the presence of catalyst reaction will complete in just 10 minutes. The silver precipitates can also be formed without using propanal as in the case of silvering of mirror when ammonia (NH₃) reacts with silver nitrate (AgNO₃) and forms ammonium nitrate but the problem is that an excess amount of ammonia (NH₃) cause these silver precipitates to get dissolves in aqueous solution. DEA has a tendency to produce hydroxyl ion which reacts with aldehydes group and forms carboxylic acid which releases an electron in the reaction that will reduce silver ion. The carboxylic acid encapsulates the newly formed silver particles stops the further growth of particles & prevent it from agglomeration with other particle.

The formed particles have very high surface energy due to high surface area but energy can also be reduce through surface relaxation, surface restructuring, surface adsorption of chemical & physical species and compositional segregation of impurities [3]. Protective layer plays a vital role in stabilizing a nanoparticle from further agglomeration. There are two types of approaches which are commonly used to protect the particle from agglomeration. Electrostatic stabilization is caused by the Columbic repulsion between particles, caused by the electrical double layer formed by ions adsorbed at the particle surface and the corresponding counter ions [2].

Steric stabilization also called polymeric stabilization which is widely used in stabilization of colloidal dispersions. During the reduction of metal salt formation of carboxylic acid offers two advantages particularly when narrow size distribution is required. It absorbs on the surface of particle provide stabilization & diffusion barrier in the growth of particle.

2. Experimental Work
The starting precursors for synthesis are Silver Nitrate, propanal and diethyl amine. The aqueous solutions with different concentrations of silver nitrate and propanal were mixed together in a calculated volume of deionized water having TDS (total dissolved solid) of 0–5mg/liter by mixing through magnetic stirrer till the solution became homogenized. A pre calculated milli molar aqueous solution of diethyl amine (DEA) was added to it quickly and stirred vigorously (Conc. of chemical used in synthesis procedure mentioned in Table.1). The color change in solution is observed after 10 to 20 minutes, from black to brown and then finally a dark gray colored higher concentrated Silver Nitrate precipitates were obtained and a yellowish-green colored suspension was obtained for lower concentration of silver nitrate.

The experiment was repeated with argon environment of 0.1–0.2 atm, in a glove box to homogenize the solution and observed that cluster of particles suspended in a solution. After filtering the mixture and washing the residue repeatedly 2 to 3 times with distilled water, the residue was collected and dried in a vacuum furnace at 50°–60°C.
This experiment consisted on 2 stages. In the first stage all the mixing of precursors were at ambient conditions of the lab at 30°C by just stirring the solution at 20–30 RPM & in the second stage a controlled environment is provided in the glove box by maintaining the inside working pressure & a jet of argon gas is provided to homogenize & stabilize the particle by removing the trapped oxygen in the solution. Physical arrangement of setup is shown in Figure 2.

Table 1. Concentrations Employed in Experiments for Different Samples

| S.No. | Conc. AgNO₃ (mM) | Conc. Propanal (mM) | Conc. DEA (mM) | Particle size SEM (±10nm) | Mean (nm) |
|-------|------------------|---------------------|----------------|-------------------------|-----------|
| 1     | 150              | 60                  | 80             | 350-300                 | 325       |
| 2     | 150              | 60                  | 80             | 325-275                 | 300       |
| 3     | 100              | 50                  | 85             | 300-250                 | 275       |
| 4     | 100              | 50                  | 90             | 300-225                 | 260       |
| 5     | 75               | 45                  | 100            | 200-150                 | 175       |
| 6     | 75               | 40                  | 100            | 200-150                 | 175       |
| 7     | 50               | 40                  | 120            | 150-100                 | 125       |
| 8     | 50               | 35                  | 120            | 150-70                  | 110       |

The concentration of AgNO₃ & DEA has an inverse relation between them. When the concentration of AgNO₃ goes on increasing & the concentration of DEA goes of decreasing the outcome is large particles size with wide distribution & vice versa.

3. Results & Discussions

The scanning electron microscope is frequently used for topographical imaging of nanoparticles. These images are typically used for investigating the size, shape, impurities & stabilization of particles. In Sample preparation, nanoparticles attached on aluminum stub using double-sided carbon tape for sample mounting, remove loose sample material by gently knocking the holder to a hard surface. Transfer the stub with sample directly to the SEM for topographical imaging. The characterization was carried in FEI SEM Quanta 200.

SEM images for the Sample No.7 (Table 1) are shown in figure 3 at magnification 10,000X & figure 4 at magnification at 20,000X. The secondary electrons results indicate that particles are nearly spherical identical in shape, dispersive & crystalline in structure. The diameters of the polycrystalline particles can be measured by using the scale represented in the each micrograph & the calculated range is written with each below mentioned figure.

Elemental compositional analysis has also been done through EDS (Energy Dispersive Spectroscopy) to find out the purity of silver nanoparticles. Since there is a huge difference in atomic number of oxygen & silver, atomic number contrast of these two element is a primarily tool in identifying the weight percentage. Results are summarized in Table 2; shows 98.06% by weight & 88.11% by atom silver nanoparticles & just 1.96% & 11.89% respectively oxygen were present. Graphically the results are represented in Graph 1 which is an automated generated graph by built-in software of SEM shows the highest counts of silver. The presence of oxygen shows that some particles got oxidized & agglomerate by forming silver oxide, but it’s a very minute quantity, rest of them are still stabilized.

Quantitatively the particle size distribution is being best evaluated through Laser Particle Analyzer characterization. To find the distribution, first run the standard solutions of known size distribution, the detectors record the energy scattered & absorbed at particular angle & makes scattering patterns then compares the values of samples with these standard values. BT-9300H Better Size Instrument had been used for particle size analysis.

Eight different samples were being run to find out the mean particle distribution of silver particles (as shown in Table 1). The recorded distribution of each individual sample is shown in the histogram.
(Graph 2), the results are on the basis of volume circulates in the chamber, for different samples assume that circulating pumps took 100% volume to exposed chamber of x-rays.

For Sample 1 in Histogram (Graph 2), Result shows out of 100%, 50% in 300-310 nm, 5% in 310-320nm, 30% in 320-330nm, 40% in 330-340nm & 5% in 340-350nm particles of silver were present, same sequence of interpretation will also be followed for the distribution of particles in sample 2,3,4,5,6,7 & 8.

Fourier Transforms Infra Radiation (FTIR) serves as the molecular fingerprint for the identification organic materials. This technique is extremely useful for the confirmation of the presence of carboxylic acid on the silver nanoparticles as a coating. The obtained FTIR spectrum of the organic material present in the sample compared for best matches with libraries of spectra that have been cataloged for known materials. There are five broad peak can be seen in the figure 5 of silver particle spectra at 3469, 2370, 1653, 1571, 1506 cm\(^{-1}\).

The first peak at 3469 & 1571 cm\(^{-1}\) must be assigned to hydroxyl group [8], because in the oxidation some of the hydroxyl group remains unreactive & also some moisture get absorb on the highly reactive surface of nanoparticles. The peak at 2370cm\(^{-1}\) belongs to (CH) stretching band of aldehyde group [9], some solution not succeeded to oxidize to carboxylic acid & the peak at 1550 & 1506cm\(^{-1}\) was concluded to be Nitrate from AgNO\(_3\), which is starting metal precursor, when we compared the standard FTIR spectra of silver nitrate.

The C=O absorption is one of the most characteristic in the spectrum. Ketone is considered the root compound while the aldehyde & carboxylic are the derived structures. The characteristic peak of carboxylic acids is present at1653 cm\(^{-1}\) is shown in the enlarged spectra of figure 6. The carboxylic acid frequency range is 1700-1300 cm\(^{-1}\). They are unique in signature, so far as the hydroxyl group has direct interaction with the carbonyl group, by the formation of a stable hydrogen-bonded structure [7].
In the enlarged spectra Figure 6, when this section compared with standard spectra all major & minor peaks should be matched, the carbonyl peaks are present with the hydroxyl group at 1571cm⁻¹, which confirm the presence of carboxylic acid on the silver particle surface.

The structure of prepared silver nanoparticles has been investigated by X-Ray Diffraction (XRD) analysis. The dry powder of the silver nanoparticles is used for XRD analysis. The diffracted intensities were recorded from 20° to 80° at 2 theta angles. The XRD pattern of the sample, prepared by the presented chemical method is shown in the Figure 7.

All diffraction peaks correspond to the characteristic crystalline Face Centered Cubic (FCC) silver lines compared with the standard powder diffraction card of Joint Committee on Powder Diffraction Standards (JCPDS), silver file No. 04–0783. No peaks from other phases are detected, indicating the high purity of silver metal. Table 3 shows the experimentally obtained X-ray diffraction angle, d spacing and the intensity count of Ag specimen.

**Particles size (nm) distribution**

**Graph 2.** Histogram of Silver Nanoparticles distribution of 8 samples.
Table 3. Shows the values observed in XRD spectrum

| Observed 2θ values | d Value Angstrom | Intensity Count | Intensity Percentage |
|--------------------|-----------------|-----------------|---------------------|
| 38.331             | 2.34634         | 1239            | 100                 |
| 44.488             | 2.03484         | 500             | 40.3                |
| 64.644             | 1.44068         | 372             | 30                  |
| 77.56              | 1.22975         | 371             | 29.9                |
| 81.751             | 1.17707         | 176             | 14.2                |
The Miller indices are calculated by using the observed $2\Theta$ values corresponding to each peak and the details are summarized in Table 4. The powdered silver nanoparticles show a cubic structure showing peaks at $2\Theta$: 38.331 (111), 44.488 (200), 64.644 (220), 77.568 (311) and 81.751 (222). The high intense peak for FFC material is (111), which is observed in the powdered sample. [8]

4. Conclusion
The Silver nanoparticles have been synthesized by wet chemical route and are characterized by using SEM, LASER Particle analyzer, FTIR spectrometry and XRD techniques. The mean particle size is found to be 120-325 nm. The concentration of DEA plays a vital role in controlling the size of particles. This work also reveals a quick route to synthesize Silver nanoparticles economically on large scale volumes using industrial grade chemicals and maintaining the purity and characteristics. In future, these Silver Nano Particles can be further analyzed for its heat transfer properties and application in nanofluids and conductive gels.

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