



Synthesis and Characterization of Silver Oxide and Silver Chloride Nanoparticles with High Thermal Stability

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In present studies, the synthesis of nanoparticles of silver oxide and silver chloride were carried out. The silver oxide nanoparticles were synthesized employing capping method while silver chloride nanoparticles were synthesized by simple precipitation of silver nitrate solution. Transmission Electron microscopic studies show that the size of silver oxide nanoparticles obtained is in the range of 2-10 nm while the size of silver chloride nanoparticles was found to be in the range of 2-12 nm. Silver chloride nanoparticles were found to be stable even at 650 °C. Thermal studies suggest that silver chloride nanoparticles behave like ionic liquid or molten salt in the range of 455-650 °C.

Key Words: Synthesis, Nanoparticles, Silver chloride, Silver oxide, Electron microscopy.

INTRODUCTION

Nanoparticles have attracted considerable interest in isolated and in consolidated forms as they exhibit unique properties that differ significantly from their coarse-grained counterparts. Metal nanoparticles have many potential applications, including use in biomedical¹, optoelectronic² and catalysis systems³ which relate to their size-dependent properties. Silver and its salts as nanoparticles are of particular interest owing to their potential applications in fuel cells⁴, heterogeneous catalysts^{5,6}, coating of medical devices⁷, sterilization of sanitary napkins⁸, anti-tumour⁹ and antimicrobial chemotherapeutic agents¹⁰, *etc.* due to which various methods of synthesis of silver salts nanoparticles and their novel applications are constantly being explored. Silver oxide has been found to possess a variety application of which a few are light transmitting adhesive film¹¹, as rechargeable cathode of secondary silver-zinc battery¹², in synthesis of Ag₅Pb₂O₆-Ag ceramics¹³, it has been used in form of paste for the manufacture of printed circuit board¹⁴, while silver chloride has been found to be applicable in measurements detecting pH change in micro-region in activated sludge or biofilm for sewage treatment electrodes for pH¹⁵, as pressure-induced superconductors¹⁶, as catalyst for stereoselective cascade alkylation/cyclization of terminal alkynes with salicylaldehydes when complexed with phosphines¹⁷, for imparting antibacterial properties in textiles.

Owing to the importance of silver salts an attempt was made to synthesize silver nanoparticles. We herein report a facile synthesis of silver oxide nanoparticles and silver chloride nanoparticles.

EXPERIMENTAL

The metal salts used have been acquired from WINLAB chemicals Ltd. (U.K.) and were used without further purification. Oleic acid and sodium hydroxide and the solvents mentioned were obtained from BDH Chemicals (England). Scanning electron microscopy (SEM) and elemental analysis (Energy Dispersive X-Ray Analysis: EDX) were carried out using Jeol SEM model JSM 6360A, while transmission electron microscopy (TEM) was carried out using Jeol TEM model JEM-1101. Powder X-ray diffraction studies were carried out using a Altima IV [Make: Regaco] X-ray diffractometer, Fourier transform infrared spectroscopy (FT-IR) was carried out using a Perkin-Elmer 1000 FT-IR spectrophotometer and thermogravimetric analysis was carried out using a Perkin-Elmer thermogravimetric analyzer⁷.

Silver chloride nanoparticles: To 200 mL silver nitrate 0.1 M solution, 0.5 M solution HCl was added until the precipitation of AgCl has seized. The greyish white precipitate obtained was filtered, washed with distilled water several times and then dried in an oven at 60 °C for 3-4 h till the AgCl is completely dry and powdery. The dried AgCl was calcined in a muffle furnace at 650 °C for 10 h. The calcined sample was then allowed to cool down and stored in a desiccator. The resulting material was then characterized by scanning electron microscopy, together with elemental analysis using (energy dispersive X-ray analysis: EDX), transmission electron microscopy, powder X-ray diffraction techniques, Fourier transform infrared spectroscopy and thermogravimetric analysis.

Silver oxide nanoparticles: Equimolar quantity of silver nitrate 4.61 g (0.0271 mol) was reacted with 8.25 g (0.0271 mol) sodium oleate to yield silver oleate. The silver oleate thus obtained was added to triethylene glycol and heated to reflux temperature while stirring continuously for about 2 h. The reaction mixture was then centrifuged for 10 min and the supernatant was discarded, the solid left at the bottom was then dispersed in hexane and stored as such. The product obtained was characterized by scanning electron microscopy, transmission electron microscopy and surface analysis (energy dispersive X-ray analysis: EDX), powder X-ray diffraction techniques, Fourier transform infrared spectroscopy and thermogravimetric analysis. A schematic representation is given in Fig. 1.

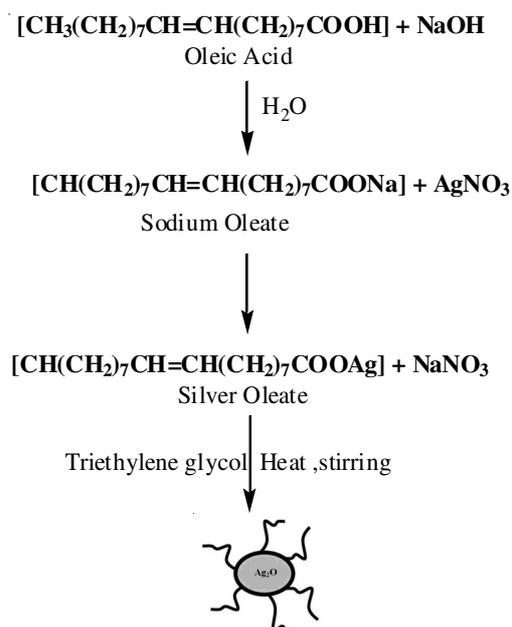


Fig. 1. Schematic presentation of formation of Ag_2O nanoparticles

RESULTS AND DISCUSSION

Microscopic studies (SEM, TEM and EDX): The scanning electron micrograph for silver oxide as shown in Fig. 2(a), suggest that the morphology, although very uniform is not well defined. The EDX studies (Fig. 2b) clearly showed the formation of silver oxide.

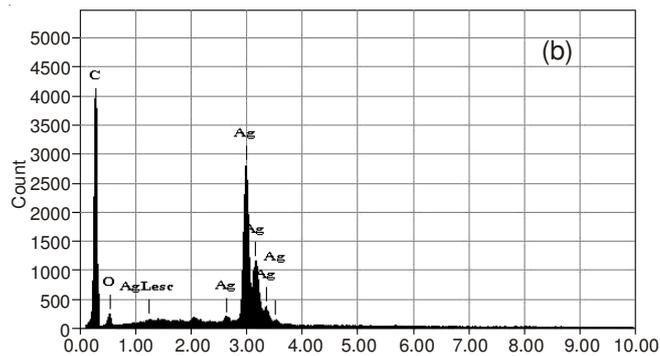
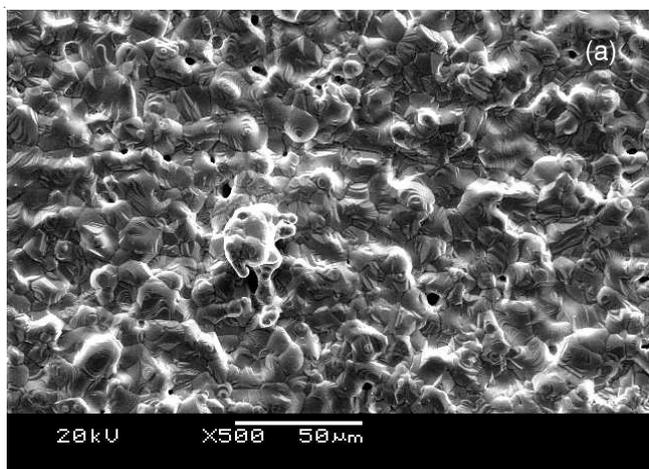


Fig. 2. (a) SEM micrograph and (b) EDX of Ag_2O nanoparticles

The transmission electron microscopic studies (Fig. 3) reveal that the silver oxide particles are well dispersed and uniform sized spherical shape. The size of the particles is found to be in the range 2-10 nm, with an average mean size of 5.44 ± 0.13 nm as shown in Fig. 4. This uniform size and shape can be attributed to the use of oleic acid as capping agent, which is reported in literature to play dual role, *i.e.* as an extractant and as a surface-capping agent that protects the outer surface of the newly formed particles thus avoiding the possibility of further growth¹⁸ and triethylene glycol as protective agent to stabilize the dispersive nanoparticles during the course of metal nanoparticle preparation.

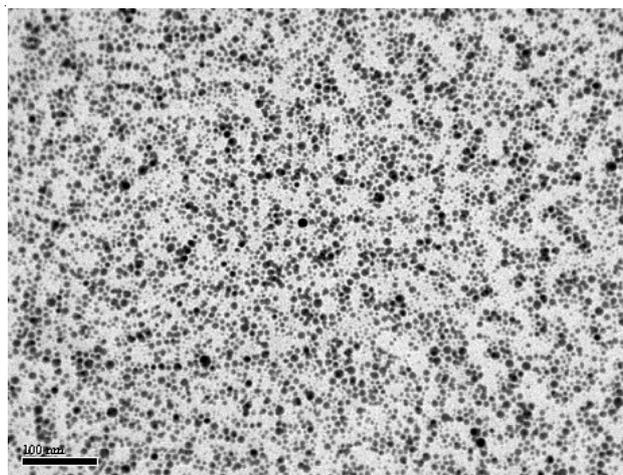


Fig. 3. TEM micrograph of silver oxide nanoparticles

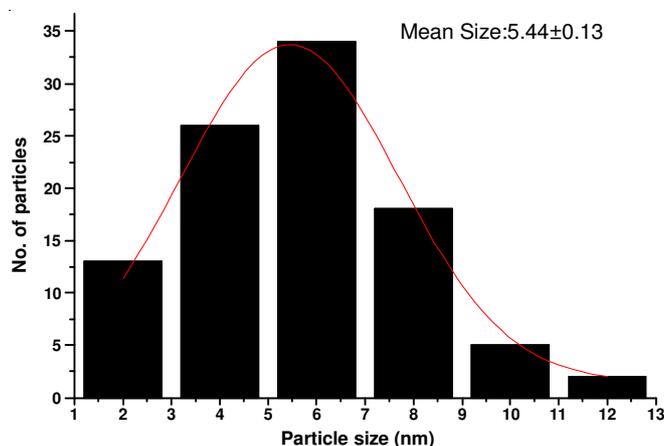


Fig. 4. Particle size distribution of silver oxide nanoparticles calculated from TEM

The most common strategy is to protect the nanoparticles with protective agents that can absorb on or bind onto the nanoparticle surface, avoiding their agglomeration thus leading to a better dispersion of uniform sized particles^{19,20}.

In an attempt to prepare Ag₂O nanoparticles by decomposition of AgCl at high temperature in the presence of oxygen, silver chloride powder, prepared by silver nitrate precipitation with HCl was kept in an oven overnight at 650 °C.

The product was characterized by scanning electron microscopy, transmission electron microscopy and surface analysis (energy dispersive X-ray analysis: EDX). The SEM studies revealed the morphology as hexagonal particles. The scanning electron micrograph is depicted in Fig. 5a. The EDX Fig. 5b studies performed on the sample showed the stoichiometric presence of AgCl and no oxygen was observed in the sample, which clearly indicates that the AgCl was stable even at the temperature.

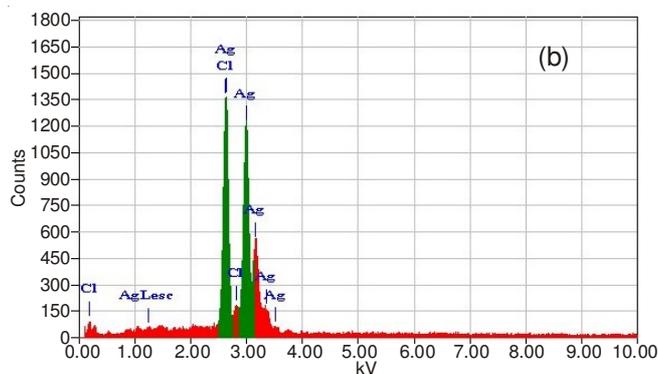
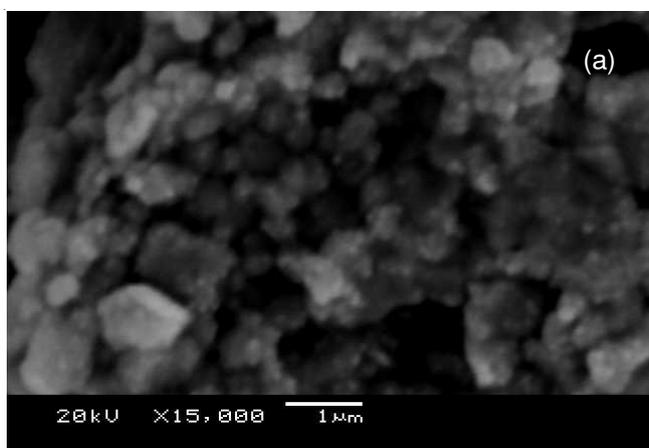


Fig. 5. (a) SEM micrograph and (b) EDX of AgCl nanoparticles

This EDX result indicated that the sample is purely AgCl and no Ag₂O was formed even after thermal treatment in air at such high temperatures. This may be because Ag₂O is less stable compared to AgCl. Ag₂O has a melting point of 300 °C compared to AgCl which has a melting point of 455 °C.

Fig. 6 depicts the TEM image of AgCl nanoparticles. Transmission electron microscopy revealed the particles which are dense and the size of these particles range from 2 nm to 12 nm. Closer look of these dense particles reveal significantly smaller nanoparticles. The sizes of these nanoparticles have been calculated and the distribution of these nanoparticles is shown in Fig. 7. This shows that the distribution is between

2-12 nm, with an average mean size of 4.16 ± 0.24 nm. AgCl nanoparticles have earlier been reported²³, synthesized by using water soluble polyelectrolyte as capping agent. They also report the formation of nanoplates of AgCl with a polygonal edge of diameter 250-300 nm.

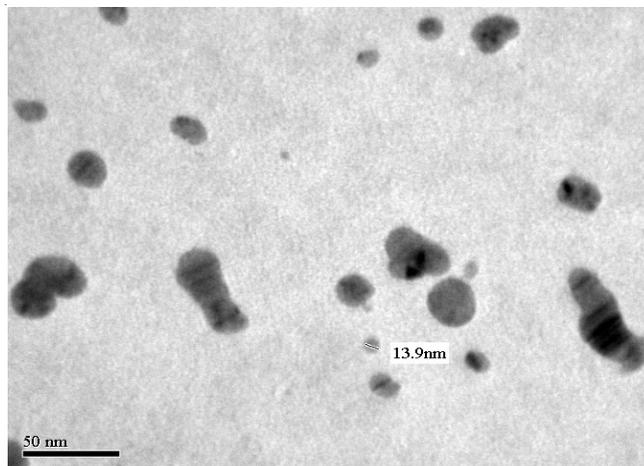


Fig. 6. TEM microgram of AgCl nanoparticles

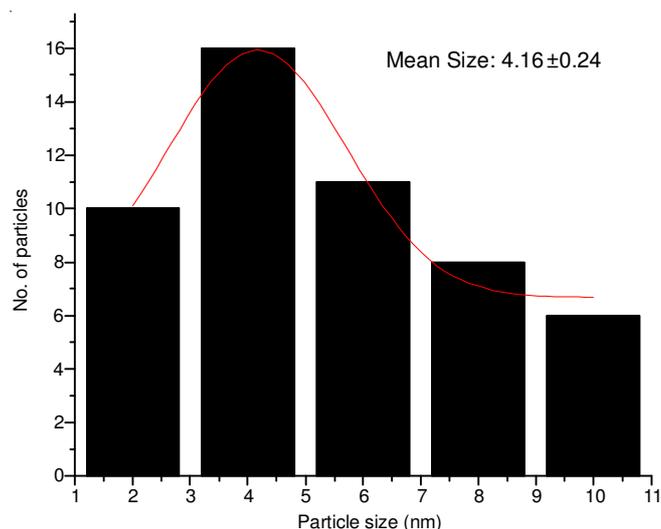


Fig. 7. Particle size distribution of AgCl nanoparticles calculated from TEM

Spectroscopic studies (XRD and FT-IR): The X-ray diffraction pattern (Fig. 8) of Ag₂O nanoparticles showed sharp reflections corresponding to the face-centered cubic (FCC) structure which is in good agreement with the reported data of Ag₂O²¹. The broadening of peaks indicates very small sizes of Ag crystallites. The crystallite size of the synthesized Ag₂O nanoparticles was also calculated from the XRD spectrum using Debye-Scherrer's equation and the size was found to be in the range 11-12 nm and this value was further supported from the calculations made on the image produced by TEM.

The XRD pattern of AgCl (Fig. 9) suggested that the structure is cubic shape, which is in good agreement with the reported data of AgCl²². The broadening of peaks indicates very small sizes of Ag crystallites. The crystallite size of the synthesized AgCl nanoparticles calculated by Debye-Scherrer's equation and the size was found to be in the range 11-14 nm. The slight discrepancy in the particle size calculation by XRD and

TEM measurements can be attributed to experimental error and also because XRD measurements are for the bulk sample.

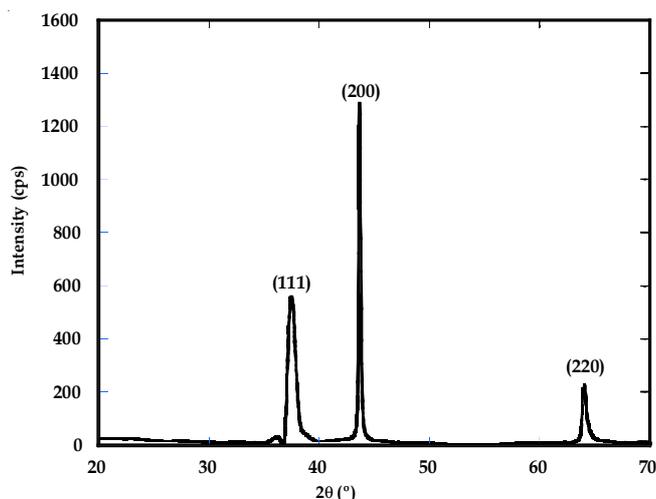


Fig. 8. X-Ray diffraction pattern of silver oxide nanoparticles

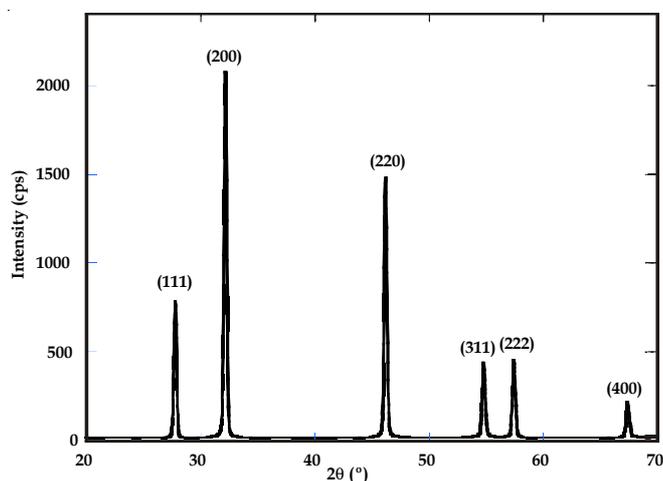


Fig. 9. X-Ray diffraction pattern of silver chloride nanoparticles

Fourier transform infrared spectroscopy spectrum of synthesized Ag_2O nanoparticles (Fig. 10) displays the characteristic band attributed to lattice vibration of silver oxide at approximately 550 cm^{-1} which was absent in the FT-IR spectrum of synthesized AgCl nanoparticles (Fig. 11).

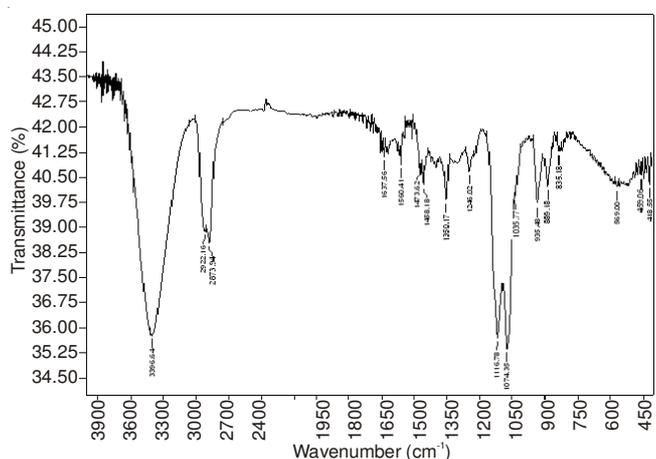


Fig. 10. FT-IR spectrum of synthesized silver oxide nanoparticles

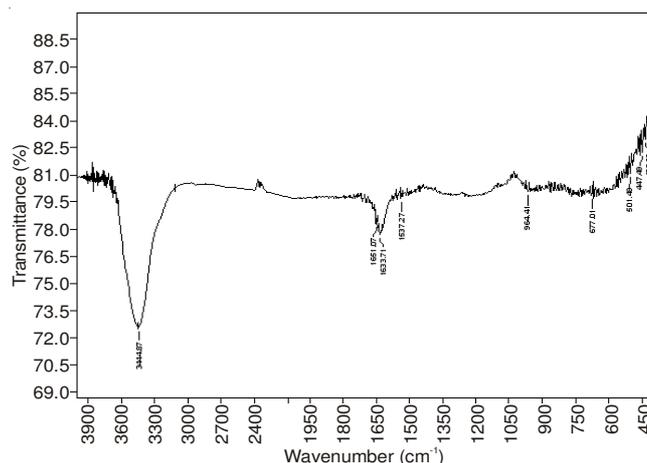


Fig. 11. FT-IR spectrum of synthesized silver chloride nanoparticles

Thermal studies: Thermogravimetric studies were carried out under nitrogen atmosphere with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$, to check the stability of AgCl nanoparticles. These studies also clearly support the stability of AgCl nanoparticles to over $650\text{ }^\circ\text{C}$. The polyelectrolyte capped AgCl nanoparticles were reported²³ to be stable only up to the melting point of AgCl which is $455\text{ }^\circ\text{C}$. The nanoparticles in the present work are not only smaller in size (2-12 nm) but also have a high thermal stability.

The TGA of AgCl nanoparticles synthesized is shown in Fig. 12. This indicates that there is no weight loss up to $650\text{ }^\circ\text{C}$ and even up to $800\text{ }^\circ\text{C}$ the weight loss is around 12%. For the total loss of chlorine in AgCl the weight loss should be 24.7%. The lower weight loss indicates that even after $800\text{ }^\circ\text{C}$ all the chlorine present in the AgCl is not lost. Further the stability of the AgCl nano particles up to $650\text{ }^\circ\text{C}$ clearly indicate that these AgCl nanoparticles act as molten salt or ionic liquids in the range of 455 to $650\text{ }^\circ\text{C}$. We have earlier synthesized low temperature ionic liquids of gold and have established a method of showing ionic liquid window from thermogravimetric studies²⁴.

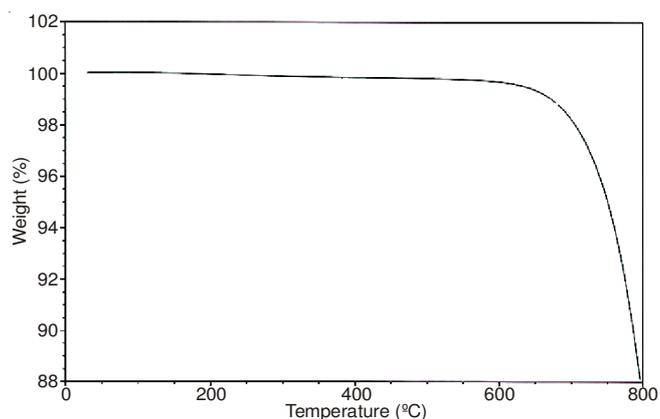


Fig. 12. Thermogravimetric analysis curve of silver chloride nanoparticles

The activities of AgCl in molten $\text{MgCl}_2\text{-KCl}$ (32.5 : 67.5 mole %) and in molten $\text{MgCl}_2\text{-NaCl-KCl}$ (50 : 30 : 20 mol %) as solvent at $475\text{ }^\circ\text{C}$ have been reported earlier²⁵. To our best of knowledge this is the first report of the behaviour of AgCl as molten salt in the range of 455 to $650\text{ }^\circ\text{C}$.

While the silver oxide particles do not exhibit such high thermal stability which can be confirmed by the TGA graph obtained. A major loss of weight at around 200 °C was observed, which is usually a trend observed with organic moieties, it suggests that the silver oxide particles are surrounded with the capping agent, which maintain the size and shape of nanoparticles synthesized (Fig. 13).

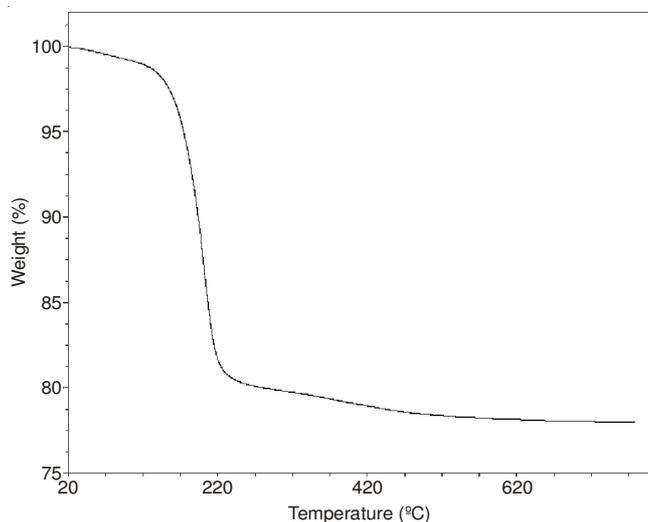


Fig. 13. Thermogravimetric analysis curve of silver oxide nanoparticles

The procedure reported here is straight forward and simple, while previous reports of AgCl nanoparticles were prepared by direct precipitation of silver ions with the surfactant counter ion in the water pools of microemulsions formed by dioctyldimethylammonium chloride in an organic *n*-decanol/*isooctane* phase.

The size of the nanoparticles was affected by various factors such as surfactant and cosurfactant concentrations, of the mole ratio of water to surfactant, R and of the loading of silver nitrate were evaluated. Increasing the surfactant concentration at fixed values of R and moles of silver nitrate resulted in a higher dependency on the reverse micellar exchange dynamics and increased the particle size²⁶. Furthermore these studies did not attempt to study the thermal stability of AgCl nanoparticles.

Conclusion

In summary, we herein report a simple facile and straight forward synthesis of Ag₂O and thermally stable AgCl nanoparticles. The AgCl nanoparticles synthesized were found to be between 2-12 nm and thermally stable up to 650 °C. These nanoparticles behave as ionic liquid in the region of 455 to 650 °C. Such high thermal stability and ionic liquid

properties may lead to new applications of these nanoparticles in catalysis and material chemistry whereas, the Ag₂O nanoparticles are not stable thermally but were found to be uniform and spherical in shape. Further studies are being carried out to find out the potential applications of the synthesized nanoparticles.

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