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ORIGINAL ARTICLE

Ionic liquid behavior and high thermal stability of silver chloride nanoparticles: Synthesis and characterization

M. Rafiq H. Siddiqui [a,*], **S.F. Adil** [a], **K. Nour** [b], **M.E. Assal** [a], **A. Al-Warthan** [a]

[a] *Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia*
[b] *Department of Chemistry, Faculty of Science, Suez Canal University, Ismailia, Egypt*

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Abstract Silver chloride was found to be stable even after calcination at 650 °C for 10 h. SEM studies revealed the morphology of silver chloride as hexagonal particles. TEM studies show the size of silver chloride particles to have an average size of 6–7 nm. Thermal studies suggest that silver chloride nanoparticles behave like ionic liquid or molten salt in the range of 455–650 °C.

1. Introduction

Silver and its salts as nanoparticles are of particular interest owing to their potential applications in fuel cells (Pishbin et al., 2007), heterogeneous catalysts (Mitsudome et al., 2009), coating of medical devices (Schierholz et al., 1998), anti tumour (Baker et al., 2005) and antimicrobial chemotherapeutic activity (Chen et al., 2006). Various methods of synthesis of silver nanoparticles and their novel applications are constantly being explored in the recent years. Silver chloride has been found to be applicable in measurements detecting pH change in micro region in activated sludge or bio-film for sewage treatment electrodes for pH (Xudong et al., 2009), as pressure-induced superconductors (Louis et al., 2004), as catalyst for stereoselective cascade alkynylation/cyclization of terminal alkynes with salicaldehydes when complexed with phosphines (Yu et al., 2009). The controlled synthesis of nanostructures with different size and morphologies is extremely important from the viewpoint of both basic science and technology (Shi et al., 2003). Silk fibre containing silver iodide nanoparticles was prepared by ultrasound using a sequential dipping method (Abbasi and Morsali, 2010). Well-defined silver chloride nanoparticles grown on the surface of PAN nanofibre were synthesized by electrospinning technology combined with gas–solid reaction (Zhang et al., 2010). We synthesized silver chloride nanoparticles by simple direct precipitation of silver nitrate with a dilute HCl solution, followed by thermal treatment.

2. Experimental

2.1. Chemicals and instrumentation

All chemicals used were obtained from BDH Chemicals (England) and used without purification. Scanning electron micros-

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[*] Corresponding author. Tel.: +966 507889048.
E-mail address: rafiqs@ksu.edu.sa (M.R.H. Siddiqui).

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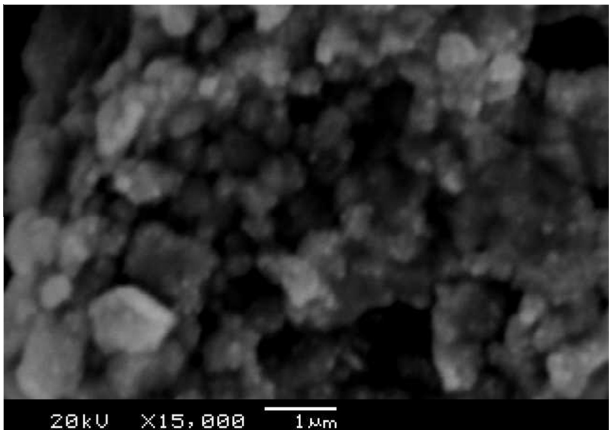

Figure 1 Scanning electron micrograph and EDX of AgCl.

copy (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 an Altima IV Rigaku X-ray diffractometer using Cu Kα radiation (λ = 1.5405 Å). Thermogravimetric Analysis (TGA) was carried out using Perkin-Elmer Thermogravimetric Analyzer 7 and Differential Scanning Calorimetry (DSC) was studied using Mettler Toledo DSC1 Star System.

For the synthesis of silver chloride nanoparticles a 200 ml silver nitrate 10 M solution was taken in a round bottom flask to which a 0.5 M solution HCl was added until the complete precipitation of silver chloride. The grayish white precipitate obtained was filtered, washed with distilled water several times and then dried in an oven at 80 °C for 8 h. The dried silver chloride was then 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 (SEM), together with elemental analysis using (Energy dispersive X-ray analysis: EDX), transmission electron microscopy (TEM), and powder X-ray diffraction techniques. The sample was subjected to TGA and DSC analysis to understand the thermal stability.

3. Results and discussion

The SEM studies revealed the morphology of silver chloride as hexagonal particles. The scanning electron micrograph is depicted in Fig. 1. The EDX studies performed on the sample showed the stoichiometric presence of silver chloride and no oxygen was observed in the sample. This result indicated that the sample is purely silver chloride and no silver oxide was formed even after thermal treatment in air at such high temperatures. This maybe because silver oxide is less stable compared to silver chloride. Silver oxide has a melting point of 300 °C compared to silver chloride which has a melting point of 455 °C.

Fig. 2 depicts the TEM image of silver chloride nanoparticles. Transmission electron microscopy (TEM) revealed the particles which are dense and the size of these particles range from 15 nm to 60 nm. Closer look of these dense particles shows significantly smaller nanoparticles. The sizes of these nanoparticles have been calculated and the distribution of these nanoparticles was calculated using the programme ImageJ as shown in Fig. 3. This shows that the distribution is between 2 and 9 nm and the average particle size is between 6 and 7 nm. Silver chloride nanoparticles have earlier been reported (Zhang et al., 2010), 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. Further confirmation of the presence of silver chloride was obtained from the powder XRD studies. All the peaks appear in the X-ray diffraction Pattern (Fig. 4) is in correspondence with that of cubic silver chloride (ICSD No. 64734). The indexing of each peak is mentioned in the figure. All the calculation of $d_{hk\ell}$ using Sherrer's equation (Patterson, 1939) was found to be 12 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.

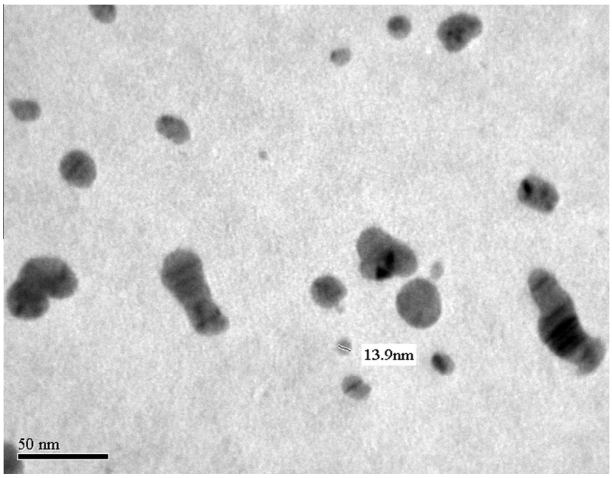

Figure 2 Transmission electron microgram of AgCl.

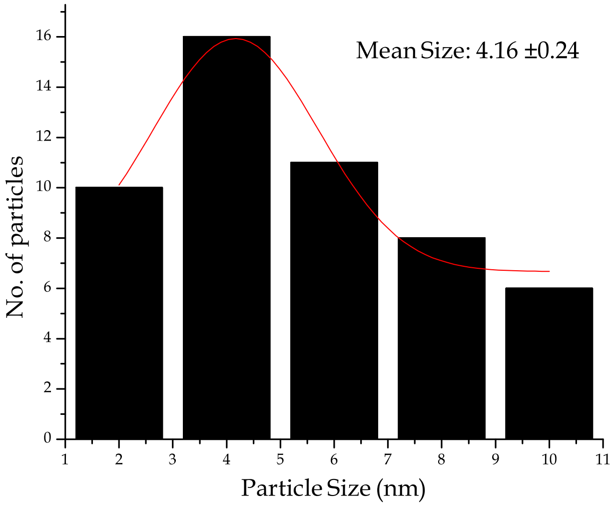

Figure 3 Particle size distribution of silver chloride nanoparticles calculated from TEM.

Thermogravimetric studies were carried out under nitrogen atmosphere with a rate of heating at 10° per minute, to check

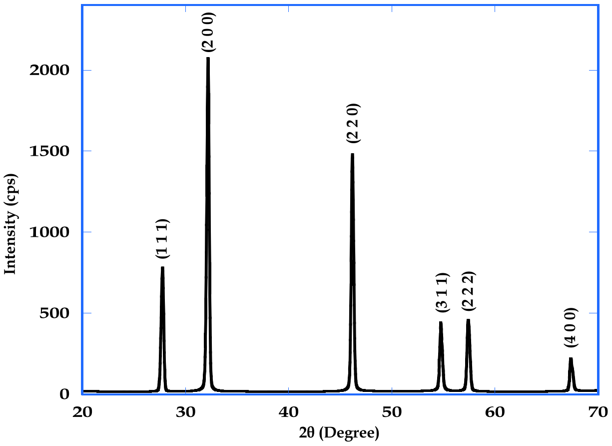

Figure 4 Powder XRD pattern for silver chloride.

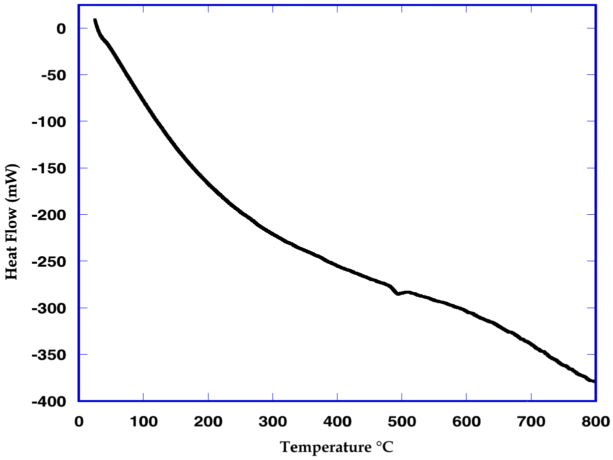

Figure 6 DSC data of silver chloride nanoparticles.

the stability of silver chloride nanoparticles. These studies also clearly support the stability of silver chloride nanoparticles to over 650 °C. The polyelectrolyte capped silver chloride nanoparticles were reported (Tiwari and Rao, 2008) to be stable only up to the melting point of silver chloride which is 455 °C. The nanoparticles in the present work are not only smaller in size (6–7 nm) but also have a high thermal stability. The TGA of silver chloride nanoparticles synthesized is shown in Fig. 5. This clearly indicates that there is no weight loss up to 650 °C and even up to 800 °C the weight loss is around 12%. For the total loss of chlorine in silver chloride the weight loss should be 24.7%. The lower weight loss indicates that even after 800 °C all the chlorine present in the silver chloride is not lost. Further the stability of the silver chloride nano particles up to 650 °C clearly indicates that these silver chloride nanoparticles act as molten salt or ionic liquids in the range of 455–650 °C, which could be confirmed by the obtained DSC plot of the AgCl nanoparticles (Fig. 6). We have earlier synthesized low temperature ionic liquids of gold and have established a method of showing ionic liquid window from thermogravimetric studies (Hasan et al., 1999). The activities of silver chloride in molten $MgCl_2$–KCl (32.5:67.5 mol.%) and in molten $MgCl_2$–NaCl–KCl (50:30:20 mol.%) as solvent at 475 °C have been reported earlier (Jindal, 1973). To our knowledge this is the first report of the behavior of silver chloride as molten salt in the range of 455–650 °C.

The procedure reported here is straight forward and simple, while previous reports of silver chloride nanoparticles were prepared by direct precipitation of silver ions with the surfactant counter ion in the water pools of micro emulsions 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 size (Maen et al., 2003). Furthermore these studies did not attempt to study the thermal stability of silver chloride nanoparticles.

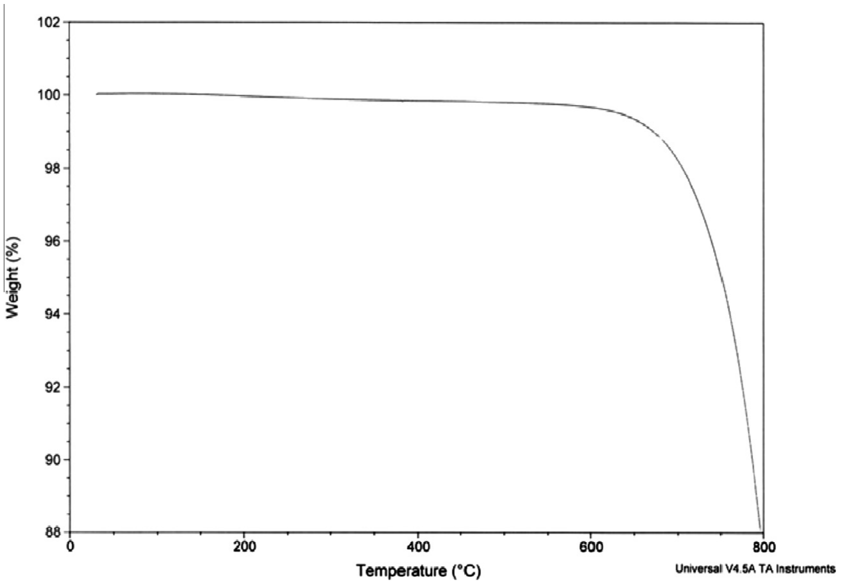

Figure 5 TGA data of silver chloride nanoparticles.

4. Conclusions

In summary, we herein report a simple facile and straight forward synthesis of silver chloride nanoparticles. The silver chloride nanoparticles synthesized were found to be in the range 6–7 nm and thermally stable up to 650 °C. These nanoparticles behave as ionic liquid in the region of 455–650 °C. Such high thermal stability and ionic liquid properties may lead to new applications of these nanoparticles in catalysis and material chemistry. Further studies are being carried out to find out the potential applications of the nanoparticles synthesized.

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