

ONE-POT SYNTHESIS AND CHARACTERIZATION OF NANO-SIZE SILVER CHLORIDE

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Silver chloride nanoparticles have been prepared by precipitation starting from silver nitrate and hydrochloric acid solutions, using different concentrations of the reactants. Their morphology and thermal behavior has been studied by SEM, XRD, TG, DTA. The synthesis resulted in AgCl particles consisting of agglomerated nanoparticles of about 50nm crystallite size.

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1. Introduction

Nanoparticles have gained considerable interest due to their high specific surfaces, electronic and optical properties, different from those displayed by their bulk-material counterparts [1]. Properties of inorganic nanomaterials depend strongly on their size and morphologies, and their design and synthesis is important for various technological applications. Due to their large surfaces, silver chloride nanoparticles found application in the degradation of organic contaminations and disinfection of water, as well as in photovoltaic cells and other optoelectronic devices [2], or biocompatible electrodes [3].

Many technologies have been explored to fabricate silver halide nanoparticles, the most common being the electrospinning and microemulsion methods [4-6]. More simple methods, such as direct co-precipitation can be used as well. Such synthesis has been done using AgNO₃ and KCl in mixed solvents of water and different alcohols, assisted by ultrasound agitation. Depending on the type of alcohol, the ultrasound power and the processing temperature, compact, spheroid particles in the size range 100-300 nm could be prepared [7]. Tiwari and Rao produced 300 nm AgCl particles using chlorinated polymer as capping agent [8]. Other solvents, for example, imidazolium ionic liquids were used to prepare AgCl micro-crystals of tunable sizes by hydrothermal method [9]. Li et al. in a facile one pot hydrothermal synthesis process achieved dendritic and flower-like AgCl microstructures of micrometer size suitable for light-driven photocatalysis [2]. An eco-friendly fabrication of silver chloride nanoparticles of 20-60 nm sizes by microbe-mediated synthesis was reported by Paulkumar et al.[10,11].

Considering the general importance of silver halides, and aiming to employ a simple preparation method, an attempt was made to synthesize relatively small silver chloride nanoparticles. We followed the recently reported method of one-pot synthesis of AgCl phase from silver nitrate solutions precipitated by hydrochloric acid solution [12,13]. In these papers Siddiqui et al. reported successful synthesis of AgCl particles of 5-10 nm average size, supported by evidence from TEM and XRD data. In our study, we used the synthesis described in [12], and

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extended it in order to tailor the properties of the resulting product, in particular, the size of the particles. For this purpose, our synthesis was carried out using different concentrations of the silver nitrate solutions and altering the order of the mixing with HCl solution. The obtained materials have been characterized for their structural properties and thermal behavior by XRD, SEM, EDS, TGA, DTA.

2. Experimental

2.1 Synthesis

The reagents: HCl 37% (S.C. Silal Trading SRL) and AgNO₃ (Reactivul Bucuresti) were used as supplied. First three samples were prepared using different concentrations of AgNO₃. Three solutions of silver nitrate of 0.1 M, 1 M and 10 M concentration (470.6 mL, 47.64 mL and 8.57 mL, respectively) were taken in three round bottom flasks. To each of them a 0.5 M solution of HCl (94.1 mL, 95.3 mL and 170 mL, respectively) was dripped slowly with stirring until the complete precipitation of silver chloride. The white precipitate was filtered, washed with distilled water several times until reaching neutral pH, and then dried in oven at 80 °C for 12 h. For better drying, the samples were further heated from room temperature to 200 °C at rate of 5°C /min and then kept at this temperature for 5 h. These samples were labeled: AgCl-0.1M, AgCl-1M and AgCl-10M, respectively.

The second series of samples was synthesized using the same reagents, but changing the order of their mixing. Silver nitrate solutions of 0.1 M, 1 M and 10 M concentration (294.12 mL, 29.41 mL and 3.53 mL, respectively) were added to 0.5 M HCl solution (58.82 mL, 58.82 and 70.58 mL, respectively), drop-wise from a burette. The white precipitate was filtered, washed and dried in the same way as the first series. These samples were named: AgCl-0.1MR, AgCl-1MR and AgCl-10MR, respectively.

2.2 Characterization

The morphology of the resulting materials has been characterized by scanning electron microscopy (SEM), and powder X-ray diffraction techniques. The samples were also subjected to thermogravimetric analysis (TGA).

Thermogravimetric and differential thermal analyses were performed on an 851-LF 1100-Mettler Toledo apparatus in air flow using alumina crucible and α -Al₂O₃ as reference substance. One sample (ca. 65 mg), dried at 80°C but not calcined at 200°C was used. The sample was heated from room temperature to 1000°C at a heating rate of 5°C min⁻¹ under air flow.

SEM imaging has been performed using a Jeol JSM 5600-LV instrument, with a IXRF Systems Inc. (USA) EDS/IXRF analysis setup. The images have been post-processed using Fotografix software.

The crystalline structure and phase composition of the powders was determined by X-ray diffraction, using a Bruker AXS D8 Discover diffractometer equipped with a Göbel mirror and a scintillation detector using Cu K α radiation. Measurements were performed over the interval 20 - 90° with a step size of 0.02° and speed of 0.15°/min. The materials were placed on a double sided adhesive tape glued to the instrument sample table. The materials were not very fine powders, but coarse grains of 100-500 μ m size, which were impossible to grind, resulting in a less than perfect precision of the sample alignment. Testing different zero positions of the sample table height showed that non-uniformity of grains did not influence the final results.

3. Results and discussion

3.1 Thermal analysis

Thermal analysis revealed high stability of the materials with practically no weight loss up to 700°C; above it chlorine starts to evaporate. At 800°C the weight loss was 1.2% and at 1000°C, the weight loss was 17%, out of the 24.7% theoretical loss expected from the full elimination of chlorine.

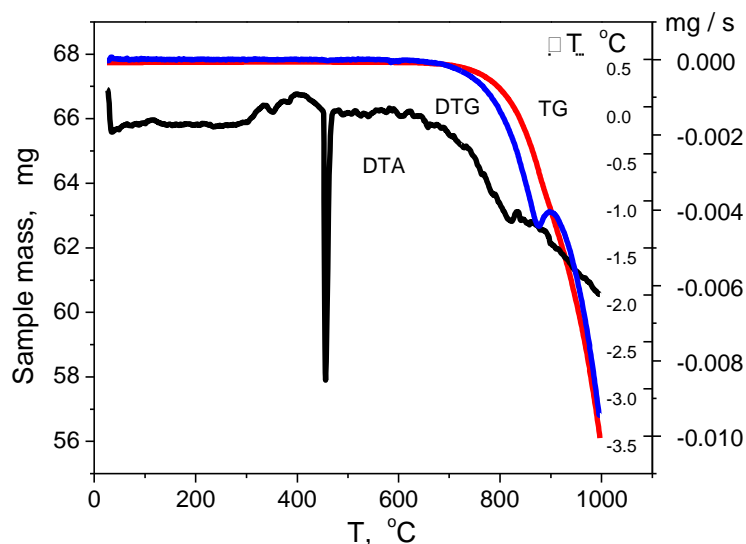


Fig. 1. TG, DTG and DTA of the sample AgCl10M

At about 460°C the melting transition can be seen on the DTA curve [8,9]. The material remains stable also above melting temperature, as there is no weight loss during the further heating in the interval 460-700°C. In this region the material becomes liquid, decomposed to silver and chlorine ions. Similar stability has been reported also by Siddiqui et al [12]. They called the state of the material above the melting temperature as ionic liquid, in analogy with the molten organic salts having low melting temperatures, called conventionally room temperature ionic liquids.

3.2 X-ray powder diffraction

The XRD measurements indicated the presence of crystalline AgCl phase (Fig. 2). Crystallite size was calculated using the whole powder pattern fitting method (WPPF) and the instrument influence has been taken into account using the diffraction pattern of a corundum standard sample recorded in the same conditions. The XRD pattern showed only the reflections of the cubic AgCl phase; neither other impurities, nor metallic Ag has been detected. The calculated crystallite sizes are given in Table 1. The values are lower limits of the realistic crystallite sizes, since the large particles and the roughness of the measured powder samples can cause an extra widening of XRD peaks resulting in smaller calculated crystallite sizes. The relative deviation of the calculated values from the realistic ones cannot exceed 20% if the sample surface roughness is smaller than 200 µm.

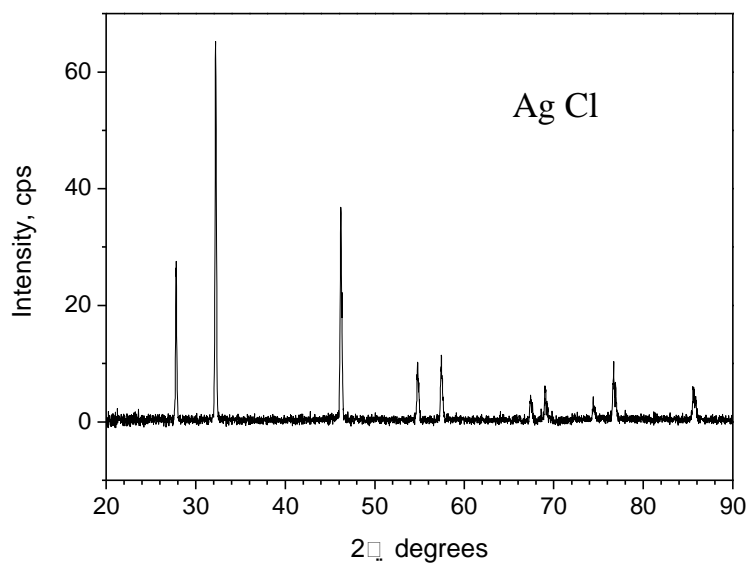


Fig. 2. XRD data of the AgCl-10M sample.

Table 1. Mean crystallite sizes as determined by XRD. The estimated uncertainty is discussed in the text

Sample	crystallite size, nm	Sample	crystallite size, nm
AgCl-0.1M	55	AgCl-0.1MR	55
AgCl-1M	44	AgCl-1MR	52
AgCl-10M	49	AgCl-10MR	60

3.3 SEM and EDS

SEM images were taken at 5000x magnification on four samples, the AgCl-0.1M, AgCl-10M, AgCl-0.1MR, and AgCl-10MR. The morphologies of several different grains of each material were nearly similar for the four investigated samples, showing aggregated particles consisting of polydisperse smaller particles having sizes of 0.5-2 μm , with pores between the particles. Four illustrative images are shown in Fig. 3. Comparing images of several grains, no systematic differences between the four synthesized samples could be revealed.

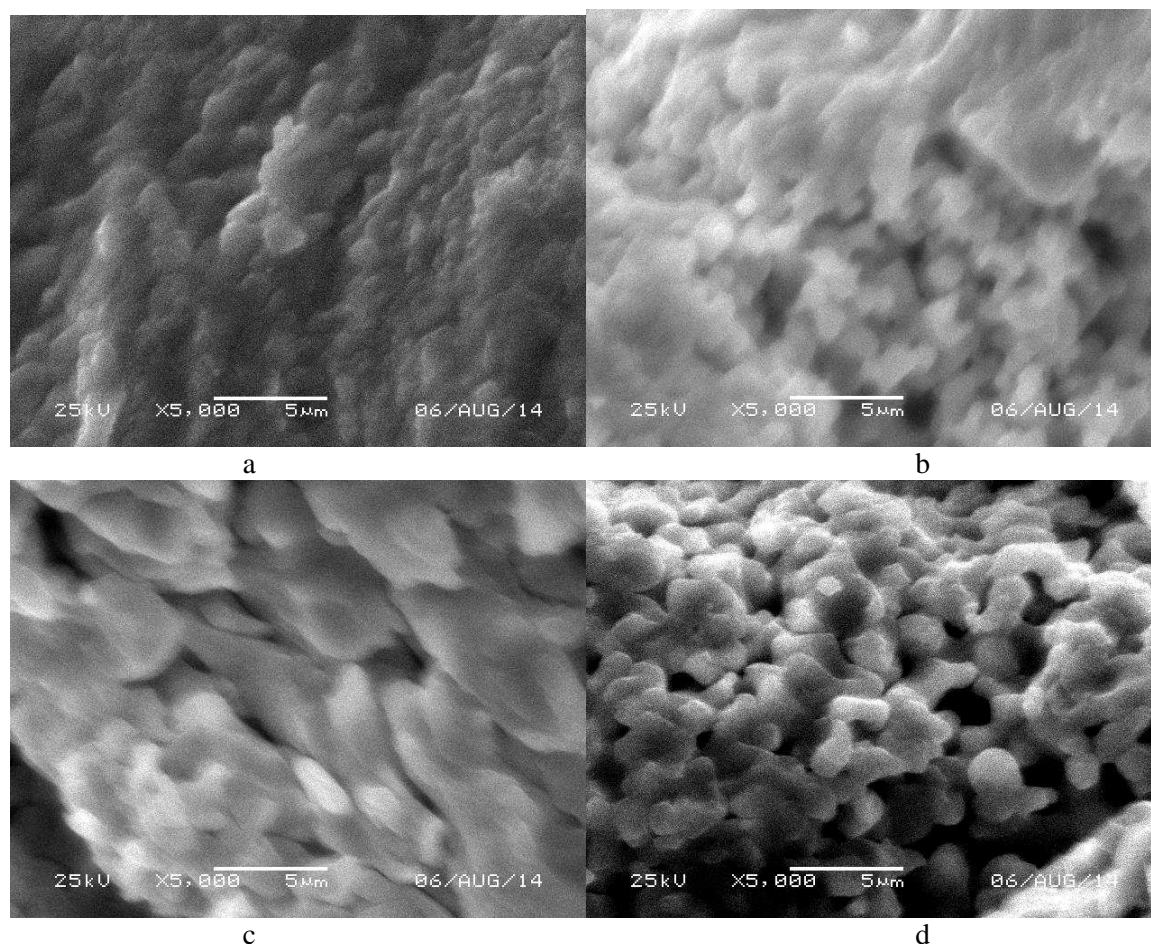


Fig. 3. SEM micrographs of samples AgCl-0.1 (a), AgCl-10 (b), AgCl-0.1R (c), AgCl-10R(d)

The elemental composition had shown Ag:Cl in atomic ratio 1.3:1, indicating that part of silver underwent reduction. It is considered to be normal, since the SEM/EDS data had been taken four weeks after the sample preparation, and there were no special precautions taken for protecting the samples, besides keeping them in dark boxes.

4. Conclusions

We have used a recently described simple synthesis method for preparation of nano-size silver chloride, precipitating silver chloride from silver nitrate and hydrochloric acid solutions. The precipitated material consisted of crystalline grains of sizes 100-500 μm . The original synthesis recipe [12] has been extended by changing the concentration of the silver salt and the order of mixing of the liquids. The morphology of the resulting silver chloride phase did not depend noticeably on concentration change within the studied range, and the mean crystallite sizes as determined by XRD were 40-60 nm, with no systematic correlation with the preparation conditions.

Although the possibility of such facile synthesis looks attractive, no other similar procedures have been found in the literature. Silver chloride particles of such small sizes of 10 nm have never been reported, besides Siddiqui et al. [12]. We conclude therefore that the reported method provides silver chloride particles of the order of 50 nm crystallite size, which aggregate in larger grains of micrometer size. More elaborated methods are necessary to decrease the particle size to the desired 10 nm. We plan to improve the one-pot precipitation synthesis method by introducing confinement in the reaction bath, using concentrated polymer solutions with mesh size of a few nanometers, expecting to obtain smaller and better separated silver chloride nanoparticles.

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