Template synthesized high conducting silver chloride nanoplates

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Abstract

Silver chloride was synthesized using a water-soluble polyelectrolyte as a capping agent. X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and differential scanning calorimetry (DSC) were employed to characterize morphology, structure and phase transition of as-prepared silver chloride. XRD, SEM and AFM confirms the formation of nanoplates of AgCl with a polygonal edge of diameter $\sim 250–300$ nm. These nanoplates are found to be thermally stable up to its melting temperature ($\sim 455$ °C) with smaller value of melting enthalpy and higher room temperature conductivity values compared to pristine silver chloride ($\sigma_{\text{Nanoplate}}/\sigma_{\text{Pristine}} \approx 10^4$).

Keywords: Nanoplates; Ionic conductivity; Silver chloride; Template; Nanoionics

1. Introduction

Nanomaterials are important class of materials due to their novel electrical, optical, magnetic and mechanical [1–13] properties for various applications such as for single electron transistors [4–5], nanoelectronics [6], lasers [7], photoelectrons, and sensors [8–13] and nanoionics [14–21].

The synthesis of nanomaterials using the concept of capping agents [22–23] is recently adapted in the field of solid-state ionics for the synthesis of shape-controlled Ag$^+$ [16–18] ion based conductors. These newly synthesized nanomaterials are found to have very interesting properties such as mesoscopic superionic conductivity at room temperature [16] and typical phase transitions [16–17]. However, only a few systems based on Ag$^+$ [16–18] ion have been investigated. Clearly, more such investigations for silver ion conductors are highly desirable to establish their general character and potential for device applications [16,21].

Silver chloride is an important dilute point defect type silver ion (Ag$^+$) conductor [24–30]. To the best of our knowledge, there is no report on the synthesis of shape-controlled silver chloride. Here we report the shape-controlled synthesis and characterization of AgCl by using a surfactant poly (diallyldimethylammonium chloride) (PDADMAC).

2. Experimental section

The 10 ml of polymer poly (diallyldimethylammonium chloride) (PDADMAC, 35 wt.% in water, Sigma-Aldrich) was added to 50 ml of ethanol and 50 ml of distilled water under vigorous stirring at room temperature. Then 1.7 g of AgNO$_3$ (Central Drug House, India, CDH Analytical Reagent) in a mixed solvent of 40 ml ethanol and 40 ml of water were added. After 60 min of stirring, the mixture was left for rest for a week at room temperature and the precipitates were collected through centrifuging the solution. The precipitates were washed carefully with water and dried at 100 °C for 2 h. A Hitachi (S-3000H) scanning electron microscope (SEM) and an atomic force microscope (AFM, Molecular Imaging, USA, having gold-coated SiN$_3$ cantilevers) were used to investigate the morphology of the precipitates. The X-ray diffraction (XRD) pattern was obtained using an X’Pert PRO PANalytical instrument with Cu K$_\alpha$ radiation. Differential scanning calorimetry (DSC) was carried out on a TA instruments (Model: SDT Q600) under nitrogen atmosphere in the temperature range of 25 °C$< T <$ 720 °C at a heating rate of 10 °C/min using alumina as a standard. The electrical measurements on the sample
(at room temperature) are performed on a uniaxially pressed
(using high chromium–high carbon steel die at a pressure
of ∼4 tons/cm²) pellet (area ∼54.11 mm² and of thickness
∼4.15 mm) by two probe measurement using SI 1260
(Schlumberger) impedance analyzer with 1296 (solartron)
dielectric interface in the frequency range of 10⁻²–10⁶ Hz.

3. Results and discussion

Fig. 1 shows a typical SEM and AFM image of the pre-
cipitate obtained as described in the experimental section at
different magnifications. Plate like nanoparticles with a
polygonal edge of diameter ∼250–300 nm are obvious from
Fig. 1a–d. The atomic force microscopy (AFM) image
(Fig. 1c–d, topography) demonstrates that the large quantity
of homogeneous nanoplates formed during precipitation.
Fig. 2a–c shows clearly the cross-section of a typical hexagonal
nanoplates which is ∼270×500 nm². Fig. 2a cross-sectional
plot shows a dip of depth ∼90 nm indicating the height of a
nanoplate from its adjacent bottom layer. The diagonal length
of a typical hexagonal nanoplates is determined by drawing a line
along the diagonal (Fig. 2b). The vertical arrows (↓) in cross-

![Fig. 1. SEM Micrograph of as-prepared AgCl nanoplates at different magnifications (a) 10 k (b) 60 k (scales are shown on the images). (c)–(d) morphologies of the as-prepared AgCl nanoplates through AFM topography obtained using capping agent PDADMAC as described in experimental section.](image-url)
Fig. 2. Cross-sectional determination of nanoplates using AFM topographical images (a) a line is drawn along the width on the nanoplate. The vertical line (↓) in the cross-sectional plot indicates the width of a typical hexagonal nanoplates ∼270 nm. However, the horizontal arrows (→) touching to y-axis indicates height of nanoplates from its adjacent bottom layer. (b) Shows diagonal length determination of a typical nanoplates. The vertical arrow (↓) in the cross-sectional plot indicates the diagonal length ∼500 nm. (c) Edge length determination of a typical hexagonal nanoplates which is ∼ab=bc ∼300 nm. (d) Three-dimensional view of the nanoplates deposited on substrates.
sectional plot of Fig. 2b shows the diagonal length of nanoplates is \(\sim 500 \text{ nm}\). Fig. 2a shows that the distance between vertical arrows is \(\sim 270 \text{ nm}\). So the cross-section of a typical hexagonal plate is \(\sim 270 \times 500 \text{ nm}^2\). Again the AFM image (Fig. 2c, \(ab=bc \sim 300 \text{ nm}\)) confirm the edge diameter of nanoplates to be \(\sim 300 \text{ nm}\). Fig. 2d shows a three-dimensional view of the nanoplate film deposited on glass substrate by drop cast method. Moreover, the EDAX study of sample shows only the presence of silver and chlorine without any other element contamination.

Fig. 3a further shows the XRD pattern of the synthesized precipitates of high purity AgCl. All the diffraction peaks can be readily indexed to an FCC phase of silver chloride with the lattice constant \(a=b=c=5.549\), \(\alpha=\beta=\gamma=90^\circ\) (JCPDS-00-006-0480 or JCPDS no.31-1238). The crystallite size is \(\sim 32 \text{ nm}\) calculated from XRD pattern using Debye–Scherrer equation. The thermal stability of as-prepared samples studied by differential thermal analyzer (DSC) (Fig. 3b). A transition to a melting phase occurs for as-prepared AgCl as obvious from Fig. 3b. It is evident that enthalpy of melting of the as-prepared AgCl is higher in heating cycle (\(\sim 83.61 \text{ J/g}\)) than that in the cooling cycle (\(\sim 70.42 \text{ J/g}\)). These fusion enthalpies are lower in magnitude with respect to the pristine silver chloride (\(\Delta H \sim 91.08 \text{ J/g}\)) [27–30]. This decrease of heat of fusion (melting) may be attributed to more disordered phase of the nanoplates. The heating cycle melting phase transition occurs at 456 °C, which is almost same for the cooling cycle phase transition temperature (\(\sim 454 \text{ °C}\)) at the heating rate of 10 °C/min.

Fig. 4a shows a typical impedance spectrum of the pressed nanoplates in the frequency range of \(10^{-2}–10^6 \text{ Hz}\). At the ambient temperature (293 K), the impedance spectrum is a depressed semicircle accompanied by a small semicircle at the low frequency end. Such non-ideal semicircular plot may be due to presence of distributions of the relaxations times [31]. The equivalent circuit may consist of a bulk resistance \((R_{dc})\) in parallel with a constant phase element (CPE) along with a grain boundary resistance \((R_g)\) with again a constant phase element in parallel as shown in the inset of Fig. 4a. The incomplete
The conductivity spectrum is very similar to those of silver iodide. In Fig. 4b, the conductivity shows dispersion. This behaviour of conductivity is quite common in disordered solids and commonly known as universal dynamic response (UDR). In summary, we have successfully synthesized nanoplates of silver ion conductor (AgCl) at ambient temperature using the concept of capping agent (a surfactant). The synthesized nanoplates are found to be highly stable and have higher conductivity (~4 orders of magnitude) with respect to the microcrystalline silver ion conductor (AgCl). Mesoscopic effect may be a reason for the enhancement of conductivity of the material. The ac conductivity spectrum of this nanomaterial has similarities with that of the disorder solids and it can be well described by universal dynamic response (UDR).

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References


Table 1

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>n</th>
<th>A (Ω⁻¹ cm⁻¹ sⁿ)</th>
<th>σₐc (Ω⁻¹ cm⁻¹)</th>
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<tr>
<td>293</td>
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<tr>
<td>333</td>
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<td>1.03×10⁻⁶</td>
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<tr>
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<tr>
<td>373</td>
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<tr>
<td>393</td>
<td>0.30</td>
<td>5.07×10⁻⁸</td>
<td>6.93×10⁻⁶</td>
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</table>

Fig. 5. The ac conductivity spectra for the silver chloride nanoplates at various temperatures. The solid line is the best-fit curve to the experimental data points according to universal dynamic response, viz., σ'(ω)=σₐc(T)+A(ω)ωⁿ, and n<1.