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Formation of silver iodide particles from thermodynamically stable clusters using ultrasonic spray pyrolysis

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Abstract

Silver iodide particles in the submicronic size domain were synthesized in the process of ultrasonic spray pyrolysis (USP) using aqueous solutions of thermodynamically stable silver iodide clusters as precursor. After the process of USP, the AgI particles were collected in water. In order to study influence of aging time on the morphological and structural properties of the AgI particles, ultra-filtration was employed to isolate solid material from solution. The scanning electron microscopy showed change from spherical to hexagonal/triangular shape and increase of average particle size of the AgI particles as a function of aging time, which is characteristic for the Ostwald ripening growth mechanism. The X-ray diffraction measurements revealed the presence of wurtzite hexagonal and zinc blende cubic AgI modifications whose abundance is also dependent on the aging time.

Keywords: Silver iodide; Electron microscopy; X-ray methods

1. Introduction

Development of synthetic procedures for preparation of AgI particles have been an area of active research mainly due to its photosensitivity and superionic conductivity.[1–3] The growth mechanism is particularly important since the sensitivity of the photographic material depends on its grain size and crystal structure. Recently, much attention has been paid to the preparation and characterization of AgI nanoparticles,[4–10] as well as structural changes of halides during the aging process.[11] On the other hand, very recently, it has been shown that small AgI clusters are in equilibrium with insoluble silver iodide if sufficient excess of iodide ions and other additives is present.[12,13]

Ultrasonic spray pyrolysis (USP) has been used for preparation of particles of desired morphology on a large scale. Recently, we showed that usage of colloidal nanoparticles as building blocks lead to formation of more organized amorphous or crystalline, two- or three-dimensional units, making them highly interesting and diverse for advanced materials.[14–17] In this paper, instead of nanoparticles we use clusters whose agglomeration number is very small as precursor in the process of USP in order to test capability of this methodology. Well-defined AgI clusters with up to 10 AgI pairs were chosen to be starting material, and bulk AgI obtained in the process of USP was characterized using optical, morphological and structural techniques.

2. Experimental

All chemicals (silver nitrate, potassium iodide, 2-propanol and toluene) were of the highest purity available and they were used without further purification. Aqueous solutions of thermodynamically stable AgI clusters, used as a starting material in the process of USP, were prepared as described in literature.[12] Briefly, 1.25 M $AgNO_3$ was combined with 5 M KI. After precipitation of AgI, supernatant solution containing thermodynamically stable AgI clusters was separated and used in further work.

The AgI powders were obtained in the process of USP using solutions containing AgI clusters as a starting material. Briefly, laboratory setup for USP consists of ultrasonic atomizer (GAPUSOL-RBI-91-012) operating at a frequency of 1.7 MHz for aerosol generation, and horizontal electric furnace with the quartz tube and a vessel for particle collection. The effective heating length of reactor tube was 1.25 m with the maximum temperature of 300 °C in the middle of the furnace. The flow rate of air was 30 l/h. The flow rate of aerosol droplets was assumed to be equal to the flow rate of gas carrier, and residence time

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of aerosol droplets in the furnace was found to be 1 min. The obtained AgI particles were collected in water. In the first series of experiments AgI particles were separated from water containing excess of KI immediately after synthesis, while in the second set of experiments aging time of AgI particles was 2 weeks. The separation process was performed using ultra-filtration through a Millipore membrane of 0.01 μm pore size.

Absorption spectra of the precursor solution, as well as solutions obtained after the process of USP were performed using a Perkin-Elmer Lambda 35 UV–vis spectrophotometer. The temperature of the solution was maintained at $25 \pm 0.1\,^{\circ}C$, while spectrophotometric cells with optical path length of 1 cm were used.

The scanning electron microscopy (SEM) measurements were performed using JEOL JSM-6460LV instrument. The solid AgI samples on a Millipore membrane were sputtered under vacuum with gold.

The X-ray diffraction (XRD) measurements were carried out on a Philips PW-1050 automatic diffractometer, using Cu Kα radiation. Measurements were performed in the 2θ range from 10° to 120° with scanning step width of 0.02° and time of 10 s/step. Computer programs for convolutive X-ray line broadening analysis by Enzo, Polizzi and Fagherazzi were used for the convolutive fitting of peaks.

3. Results and discussion

We recently showed that clusters containing up to 10 AgI pairs in aqueous solution are in equilibrium with the insoluble silver iodide if sufficient excess of iodide ions is present.[12] We expect that the synthesis of powders by using the process of USP and AgI clusters as a starting material enables formation of very homogeneous AgI powders inside the reactor. During the process of USP the sprayed droplets containing AgI clusters are transformed into microporous or dense particles by different processes, including solvent evaporation and in our case evaporation of NO_3^- ions. In the first series of experiments AgI particles were isolated from solvent containing excess of KI immediately after synthesis, while in the second set of experiments aging time of AgI particles in water was 2 weeks. The ultra-filtration was used to separate AgI powders from solutions.

Absorption spectra of the precursor solution and dispersion in water obtained after the process of USP are shown in Fig. 1. Featureless absorption spectrum of AgI clusters (curve a) is the same as already shown spectrum in literature.[12] As we expected, absorption spectrum of dispersion in water obtained after the process of USP (curve b) showed typical features of bulk AgI with an excitonic peak around 422 nm.[8] It is obvious that long wavelength tail is a consequence of light scattering due to large size of AgI particles. Solution obtained after ultra-filtration does not show any absorbance, except in the wavelength regime close to far UV spectral range due to the presence of iodide ions. Further, we will concentrate on morphology and structure of bulk AgI obtained by the process of USP and isolated by ultra-filtration.

SEM images of the AgI samples obtained immediately after the process of USP and after the aging of 2 weeks in water are shown in Fig. 2A and B, respectively. Sample obtained immediately after the process of USP mostly consists of spherical particles with diameter smaller then 100 nm (Fig. 2A). SEM image of the AgI sample aged 2 weeks in water (Fig. 2B) consists of AgI particles with hexagonal/triangular shape. Particles

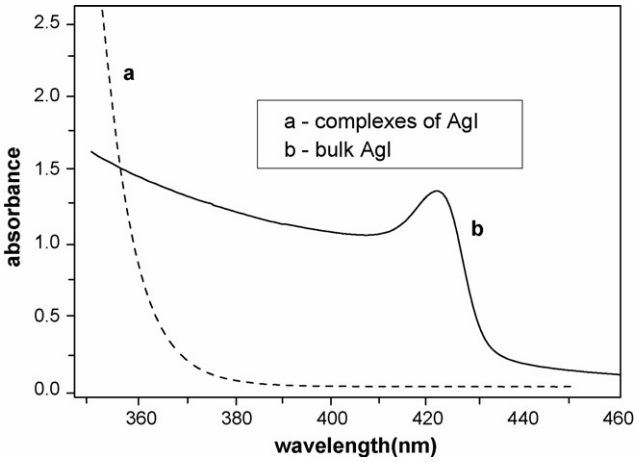

Fig. 1. Absorption spectra of precursor (a) and AgI particles collected in water after the process of USP (b).

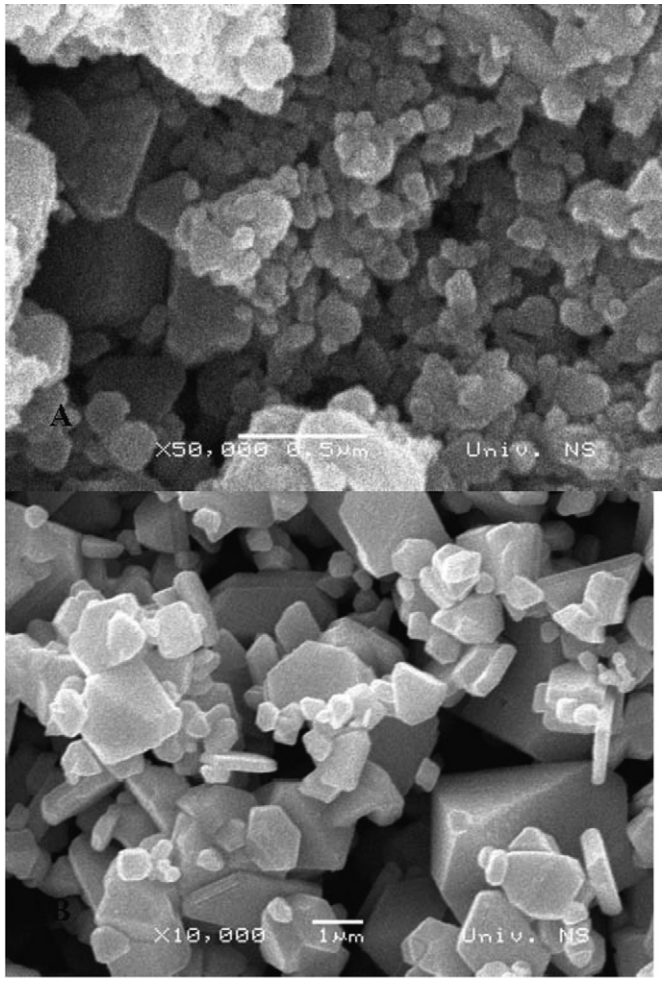

Fig. 2. SEM images of AgI particles immediately after the process of USP (A) and after 2 weeks of aging in water (B).

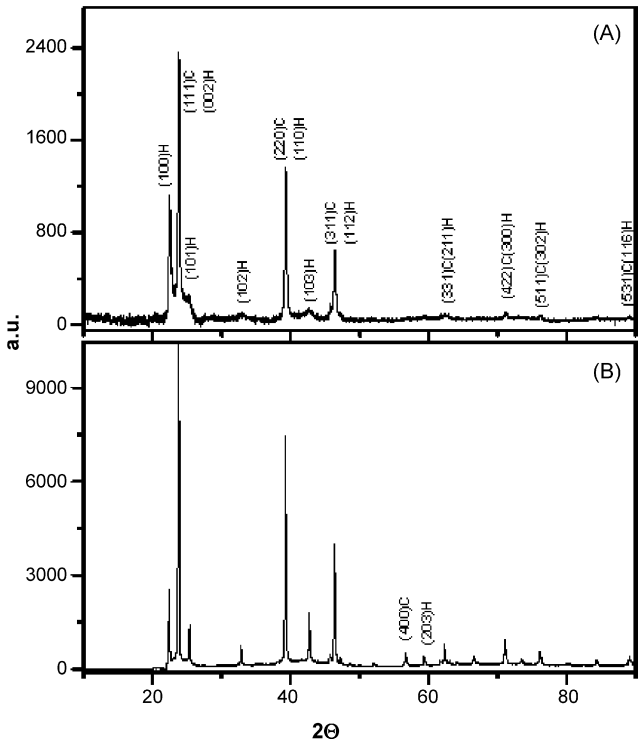

Fig. 3. The XRD patterns of AgI particles immediately after the process of USP (A) and after 2 weeks of aging in water (B).

are significantly larger, in the micron or sub-micron size scale. The disappearance of small spherical particles as well as very broad size distribution of aged sample indicates growth of large particles on the expense of small ones, i.e. Ostwald ripening growth mechanism.

The experimentally observed XRD pattern of the AgI powder deposited from water on the filter immediately after the process of USP is shown in Fig. 3A. It can be noticed that at room temperature and under atmospheric pressure two AgI phases coexist, hexagonal (β-AgI) and cubic phases (γ-AgI), having wurtzite and sphalerite structure, respectively. Hexagonal phase dominates in the XRD pattern of AgI obtained immediately after the process of USP (Fig. 3A), while the XRD pattern of AgI after 2 weeks of aging (Fig. 3B) indicate increase of the content of cubic phase (peaks attributed only to the cubic phase at 56.72 and 62.31 are more pronounced), although the hexagonal phase is still dominant. The hexagonal phase is less thermodynamically stable than the cubic according to recent theoretical calculations,[18] and consequently aging leads to transformation of hexagonal into cubic phase. We performed a convolutive fitting of peaks (see Section 2) and found by comparing relative intensities from fitted data with known JCPDS-data that the (1 0 0) and (1 0 1) direction of the hexagonal phase are the most pronounced.

In this work, we showed that by using solution consisting of thermodynamically stable AgI clusters as precursor and the process of USP as a method it is possible to synthesize AgI particles in micron and sub-micron size range. To the best of our knowledge, clusters of such a small agglomeration number were the first time used as starting material in the process of USP. Described methodology provides possibility to study influence of different solvents and aging time on the morphological and structural properties of variety of inorganic particles prepared by the process of the USP and having exactly the same history. Experiments in that direction are currently under way in our laboratories.

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