A novel method for large-scale synthesis of AgI nanoparticles

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Thiol-derivatised I–VII nanoparticles of AgI (7–16 nm) are prepared in large quantities by the reaction of silver nitrate with potassium iodide containing 1-thioglycerol in aqueous solution.

Solid electrolytes with high ionic conductivity have drawn much attention because of the possibility for applications in solid-state battery and chemical sensing systems. Recently, we have found that the ionic conductivity of polycrystalline pellet of AgI increased significantly when the particle size is decreased from the bulk to 140 nm.[1,2] Following this finding the synthesis of large amounts of small AgI nanoparticles is strongly desirable. Several wet chemical methods such as the use of gelatin[3] or polymer,[4–7] control release of iodide ions from CH_2I_2[8,9] have been studied. However these methods were all applied to very diluted solutions ($<10^{-3}$ M), and thus AgI can not be separated as a solid powder in large quantities. Here, we report the synthesis of a large amount of AgI nanoparticles using 1-thioglycerol (TG) as the size controller. This is the first extension of the use of thiolates in the synthesis of II–VI nanoparticles[10] to I–VII nanoparticles.

In order to grow AgI clusters with simultaneous attachment of a thiol monolayer on the particle surface, silver ions are injected in the iodide solution containing thiols maintaining $[Ag^+] = [I^-] + [TG]$. The size of the particles can be controlled by the $[I^-]/[TG]$ ratio. For a typical preparation with a $[I^-]/[TG]$ ratio of 9.0, 20 ml of a 0.2 M $AgNO_3$ solution was rapidly added into a solution containing 18 ml 0.2 M KI and 2 ml 0.2 M TG under vigorous stirring. After 20 min of reaction, the resulting turbid yellow solution was sealed into cellulose tubing (Type 24/32, pore size 2.4 nm, Visking company) and dialysized against flowing water for 24 h in the dark. The pH of the solution changed from 2.13 to 7.16. After freeze drying, 0.92 g of yellow powder which corresponds to a yield of 98% was obtained. Fig. 1 shows the electron micrograph (recorded with Hitachi 8100 instrument at 200 kV) of the AgI particles sampling from a 200 times diluted initial solution. The particles were spherical with a mean diameter of 16 nm but characterized by a wide size distribution (standard deviation of 9.4 nm, calculated from the digitalized image with a NIH software package). The morphology of these particles is different from that prepared by simply mixing $AgNO_3$ and KI in dilute solutions[4,5] which often shows the shape of regular triangles with rounded corners or irregular polygons. This difference indicates that thiolates can effectively inhibit the anisotropic growth of the special crystal plane of AgI nuclei, leading to the formation of small particles even in concentrated solutions.

Fig. 2 shows a typical electron diffraction pattern of the sample in Fig. 1. The strong diffraction spots indicate that the samples are polycrystalline, this is also confirmed by HRTEM image in the insert of Fig. 1. The measured lattice spacings calibrated with a standard gold film were 3.969 (100), 3.737 (002), 3.483 (101), 2.723 (102), 2.296 (110), 1.954 (112), 1.326 (300) and 1.249 Å (302) of β-AgI (wurtzite structure). Also, the spacings at 3.737 (111), 2.296 (220), 1.949 (311), 1.673 (400), 1.480 (331) and 1.249 Å (511) can be attributed to γ-AgI (zinc blende structure). The existence of only these two types of diffraction rings indicates that the particles are composed of only β- and γ-AgI.

X-Ray diffraction spectra of the solid powder (recorded with a Rigaku RINT/Dmax-2000 diffractometer) confirmed the above assignment (Fig. 3). All diffraction peaks show broadening compared to that of the bulk sample. The average particle size was 15 nm estimated from the Scherrer's equation. Further simulation of the XRD pattern with a Rietveld method, utilizing a program RIETAN-94 developed by Izumi[11] revealed that the

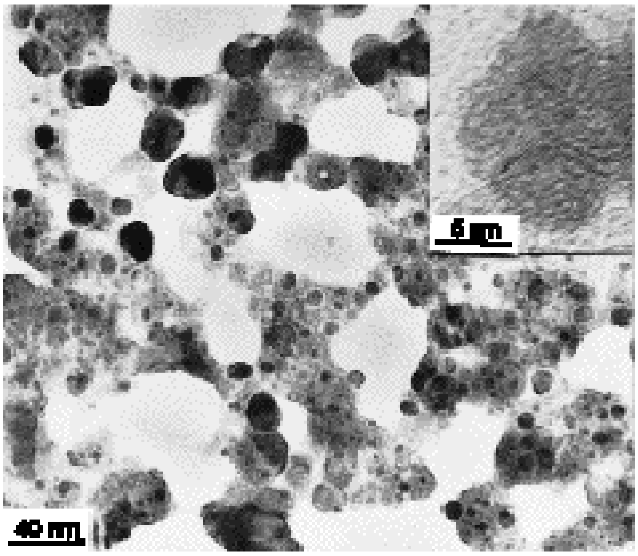

Fig. 1 Transmission electron micrograph of AgI particles prepared with an initial $[I^-]/[TG]$ ratio of 9.0. The insert shows a high resolution TEM image of one particle.

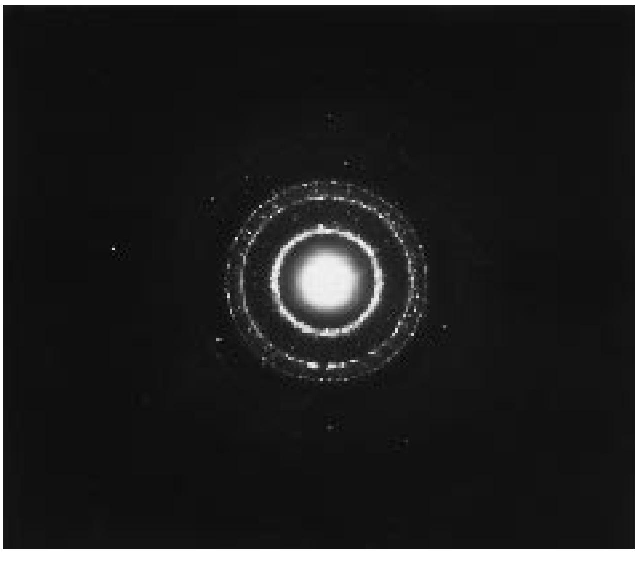

Fig. 2 Electron diffraction pattern of the sample in Fig. 1

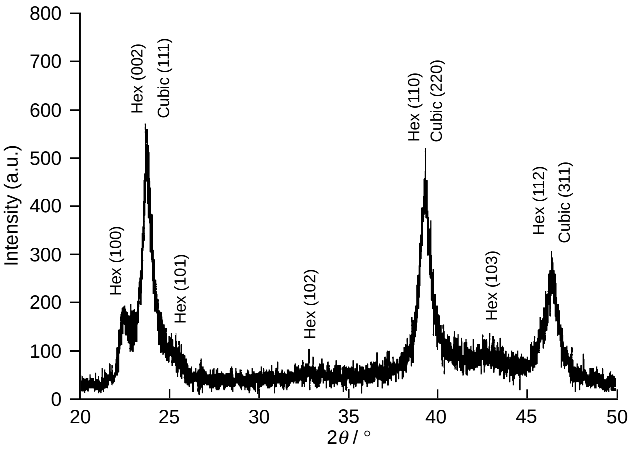

Fig. 3 X-Ray diffraction pattern of the sample in Fig. 1

particles contain 36.5% of β- and 63.5% of γ-AgI. According to the theoretical dependence of X-ray diffraction peak intensity ratio, *R*, on the amounts of hexagonal and cubic AgI proposed by Berry (Fig. 1 in ref. 3, where *R* is the relative ratio of intensity of the center line of the diffraction triplet to the sum of intensities of the two outside lines, $[I(111)_{\text{cubic}} + I(002)_{\text{hex}}]/[I(100)_{\text{hex}} + I(101)_{\text{hex}}]$), a consistent result of 40.0% of β- and 60.0% of γ-AgI can be deduced.

The IR spectrum of the particles is similar with that of TG except for the absence of the S–H vibration peak at 2558 cm^{-1}. This phenomenon is also observed for other AgI particles prepared with lower $[\text{I}^-]/[\text{TG}]$ ratios, which contain more organics (up to 30.4%). Also, the resulting AgI solution is acidic (pH = 2.13). This shows that the following chemical reaction occurred (TG = R–SH):

$$\text{R–SH} + \text{Ag}^+ \text{ (surface)} \longrightarrow \text{R–SAg (surface)} + \text{H}^+ \qquad (1)$$

The thiolates are connected to the Ag^+ sites on the AgI particle surface *via* sulfur atoms, and act as the 'skin' of the AgI particles. Energy-dispersive X-ray microanalysis (Kevex system attached to Hitachi 8100) gave: Ag, 50.0; I, 45.2%. Thermogravimetry showed a 4.2% mass loss after heating the powder to 400 °C under a nitrogen atmosphere. If we assume that only the organics was lost after heat treatment (XRD confirmed that the residues were mainly AgI), about 88% of the organics were removed. After heating, the yellow powder turned black and bulk-like, with S still detected by EDX. This is reasonable owing to its strong interaction with silver ions. Upon decreasing the initial $[\text{I}^-]/[\text{TG}]$ ratio from 9.0 to 0.67, the size of the AgI particles decreased to *ca*. 7 nm as determined from XRD measurement, while the organic content increased to 30.4%.

We propose that this new method may find applications in large-scale synthesis of other I–VII nanoparticles such as AgBr or CuCl. Heat treatment may remove most of the organic layer. This suggests great potential in further increasing the electric conductivity of solid electrolytes by using nanometer sized AgI particles and futher work is under way.

This work was supported in part by Grant-in-Aids for Scientific Research on Basic Research (A: 09304068) and on Priority Areas (09215234), and a Grant-in-Aid for JSPS fellow from Ministry of Education, Science, Sports and Culture, Japan. One of us (S. C.) gratefully acknowledges a grant from the Japan Society for Promotion of Science for the postdoctoral fellowship.

Footnote and References

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Received in Cambridge, UK, 28th July 1997; 7/05420C