

AgI Nanoparticles: Size-Controlled Stabilization of Superionic Phase to Room Temperature

Solid-state ionic conductors are actively studied for their large application potential in batteries and sensors. From the viewpoint of future nanodevices, nanoscaled ionic conductors are attracting much interest. Silver iodide (AgI) is a well-known ionic conductor whose high-temperature α -phase shows a superionic conductivity greater than $1 \Omega^{-1}\cdot\text{cm}^{-1}$. Below 147°C , α -AgI undergoes a phase transition into the poorly conducting β - and γ -polymorphs, thereby limiting its applications.

We have recently reported the facile synthesis of variable-size AgI nanoparticles coated with poly-*N*-vinyl-2-pyrrolidone (PVP) and the controllable tuning of the α - to β -/ γ -phase transition temperature ($T_{\text{c}\downarrow}$) [1]. When the size approaches 10-11 nm, the α -phase survives down to 30°C - the lowest temperature for any AgI family material. Moreover, the conductivity of 11 nm β -/ γ -AgI nanoparticles at 24°C is $\sim 1.5 \times 10^{-2} \Omega^{-1}\cdot\text{cm}^{-1}$ - the highest ionic conductivity for a binary solid at room temperature.

Ionic conductors are crucial for operating electrochemical devices, such as batteries and sensors. Although liquid phases principally give high ionic conductivity, solid-state materials are much more suitable from the perspectives of device fabrication (facile shaping, patterning and integration), stability (non-volatility) and safety (non-explosiveness). Silver-based ionic solids are excellent candidates of electrolytes for solid state batteries both because of their high conductivity and the high polarizability of Ag^+ ions that brings high exchange rate at the electrode reaction [2]. Actually, prototypes of all-solid batteries employing silver ionic conductors have been reported [3]. However, the performance of such devices is still in need of improvement for satisfying commercial applications. Efforts to obtain a high conductivity at lower temperatures have focused on the synthesis of ternary phases derived from AgI, of metal halide solid solutions, and of inorganic composite materials. An alternative way to attempt to stabilize the superionic phase at lower temperatures can be through the fabrication of nanoscaled AgI materials with controlled size and shape. For instance, when the size of materials is down to nanoscale, the temperatures of fusion and order-disorder phase transitions can be lowered as the proportion of surface atoms increases, resulting in the increase of surface energy.

Our aim in this work was to investigate in a systematic way the size effect on T_{c} in AgI nanoparticles without any pre-shaped inorganic mold, but with the application of a soft organic polymer as a stabilizer.

We successfully synthesized PVP-coated AgI nanoparticles in a variety of particle sizes by a solution-based technique.

Figure 1 shows the extracted size dependence of the phase transition temperatures from the differential scanning calorimetry (DSC) measurements of as-prepared AgI nanoparticles measured on cooling. The size dependence of the α - to β -/ γ -phase transition temperature $T_{\text{c}\downarrow}$ is very pronounced and $T_{\text{c}\downarrow}$ shifts considerably to lower temperatures with decreasing nanoparticle size, leading to a progressively enlarged thermal hysteresis. Specifically for the 10 and 11 nm nanoparticles, $T_{\text{c}\downarrow}$ is drastically suppressed down to $40 \pm 1^\circ\text{C}$.

Detailed insight into the phase transition behavior of AgI nanoparticles was obtained from the temperature-dependent synchrotron X-ray powder diffraction at beamline BL02B2. Figure 2(a) shows the temperature evolution of the α -AgI fraction for 11 nm nanoparticles during the first thermal cycle, as derived from Rietveld refinements of the diffraction data. The results clearly show the same huge hysteresis observed by DSC, as shown in Fig. 2(b). The dominant structure of the as-prepared AgI nanoparticles at 21°C is the γ -polymorph (64.1(1)%). The β -polymorph (35.9(1)%) is also present. This phase assemblage remains stable on heating up to 138°C . Further heating leads to a gradual transformation to the α -phase that is complete at 165°C . Between 165 and 190°C , only α -AgI was observed. However, the β -/ γ - to α -phase transition is strongly thermally hysteretic. On cooling, small fractions of β - and γ -phases appear initially at 128°C and grow only slightly down to 42°C , where the

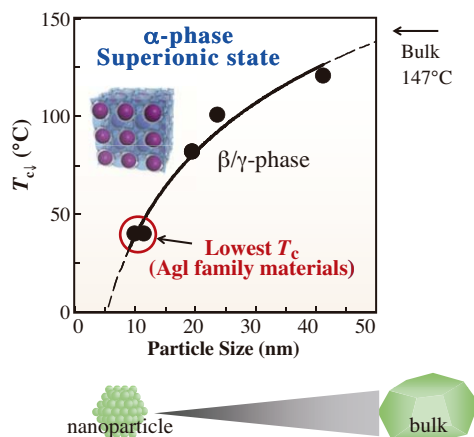


Fig. 1. Size dependence of phase transition characteristics in AgI nanoparticles on cooling. The mean diameters of the nanoparticles were extracted from the TEM images to be 9.9 ± 2.4 , 11.3 ± 3.8 , 19.4 ± 3.7 , 23.6 ± 7.3 and 41.2 ± 7.8 nm.

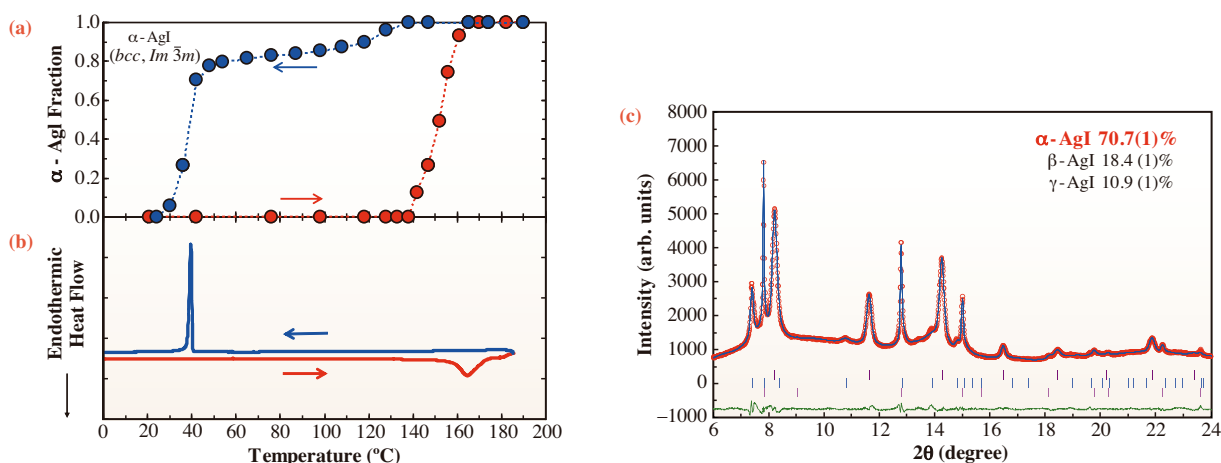


Fig. 2. Structural characterization of 11 nm AgI nanoparticles. (a) Temperature dependence of α -AgI fractions for the first thermal cycle, as extracted from Rietveld refinements of synchrotron X-ray diffraction data. (b) DSC thermograms for first thermal cycle. (c) Final observed (red circles) and calculated (blue solid line) synchrotron X-ray ($\lambda = 0.5122 \text{ \AA}$) powder diffraction profiles at 42°C following heating to 190°C and subsequent cooling (agreement factors: $R_{\text{wp}} = 2.30\%$ and $R_{\text{exp}} = 4.44\%$). The lower solid lines show the different profiles and the tick marks show the reflection positions of α -AgI (top), β -AgI (middle) and γ -AgI (bottom) phases.

α -phase is still the dominant structure (α -phase 70.7(1)%, β -phase 18.4(1)%, and γ -phase 10.9(1)%) (Fig. 2(c)). Below this temperature, which coincides with the sharp endothermic peak observed in DSC, α -AgI rapidly begins to transform into β -AgI but survives down to 30°C (Fig. 2(a)). The structural transition is complete at 24°C .

Figure 3 shows the results of conductivity measurements for 11 nm AgI nanoparticles and AgI polycrystals. The huge thermal hysteric behavior observed in DSC and diffraction measurements is also evident in the temperature dependence of the conductivity σ . We also note that the room-temperature conductivity for as-prepared 11 nm nanoparticles is significantly increased to $\sim 1.5 \times 10^{-2} \Omega^{-1}\text{cm}^{-1}$. To the best of our knowledge, this is the highest ionic conductivity reported for a binary solid at room temperature and is five orders of magnitude higher than that of AgI

polycrystals ($\sim 1.6 \times 10^{-7} \Omega^{-1}\text{cm}^{-1}$). On heating of the as-prepared nanoparticles, σ gradually increases and a notable change is observed at around 160°C , where both DSC and diffraction show a thermal event. On cooling, σ remains very high, which is consistent with the presence of superionic supercooled α -AgI whose activation energy is 0.06 eV, comparable to that of bulk α -AgI (~ 0.05 eV). Finally, σ approaches the same value as that in the heating process at 36°C .

The solution-based chemistry using PVP as a stabilizer that has been employed here is sufficiently suitable for isolating new families of nanoscaled (super)ionic conductors with controlled size and morphology. This will facilitate a wide range of fundamental studies about ionic mobility at the nanoscale at a previously inaccessible temperature window and promises applications in nanobatteries or other electrochemical devices.

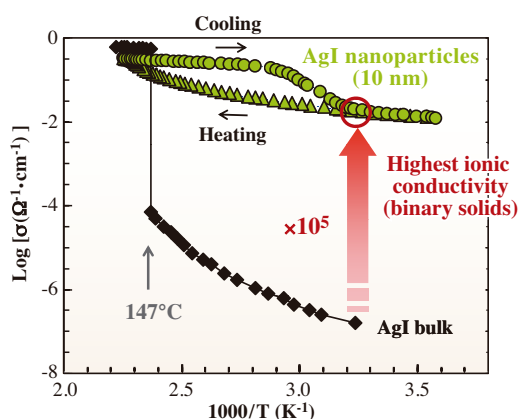


Fig. 3. Transport behavior of 11 nm AgI nanoparticles. Temperature dependence of conductivity σ for first thermal cycle. The activation energies derived using an Arrhenius expression are indicated. The conductivity data for AgI polycrystals are also included for comparison.

Rie Makiura^{a,b,*}, Hiroshi Kitagawa^{a,b,c,d} and Kenichi Kato^e

^a Department of Chemistry, Kyushu University

^b JST-CREST

^c Department of Chemistry, Kyoto University

^d INAMORI Frontier Research Center, Kyushu University

^e SPring-8 / RIKEN-JASRI

*E-mail: r-makiura@21c.osakafu-u.ac.jp

[†] Present address: Nanoscience and Nanotechnology Research Center, Osaka Prefecture Univ.

References

- [1] R. Makiura, T. Yonemura, T. Yamada, M. Yamauchi, R. Ikeda, H. Kitagawa, K. Kato and M. Takata: *Nature Mater.* **8** (2009) 476.
- [2] S. Hull: *Rep. Prog. Phys.* **67** (2004) 1233.
- [3] B.B. Owens: *J. Power Sources* **90** (2000) 2.